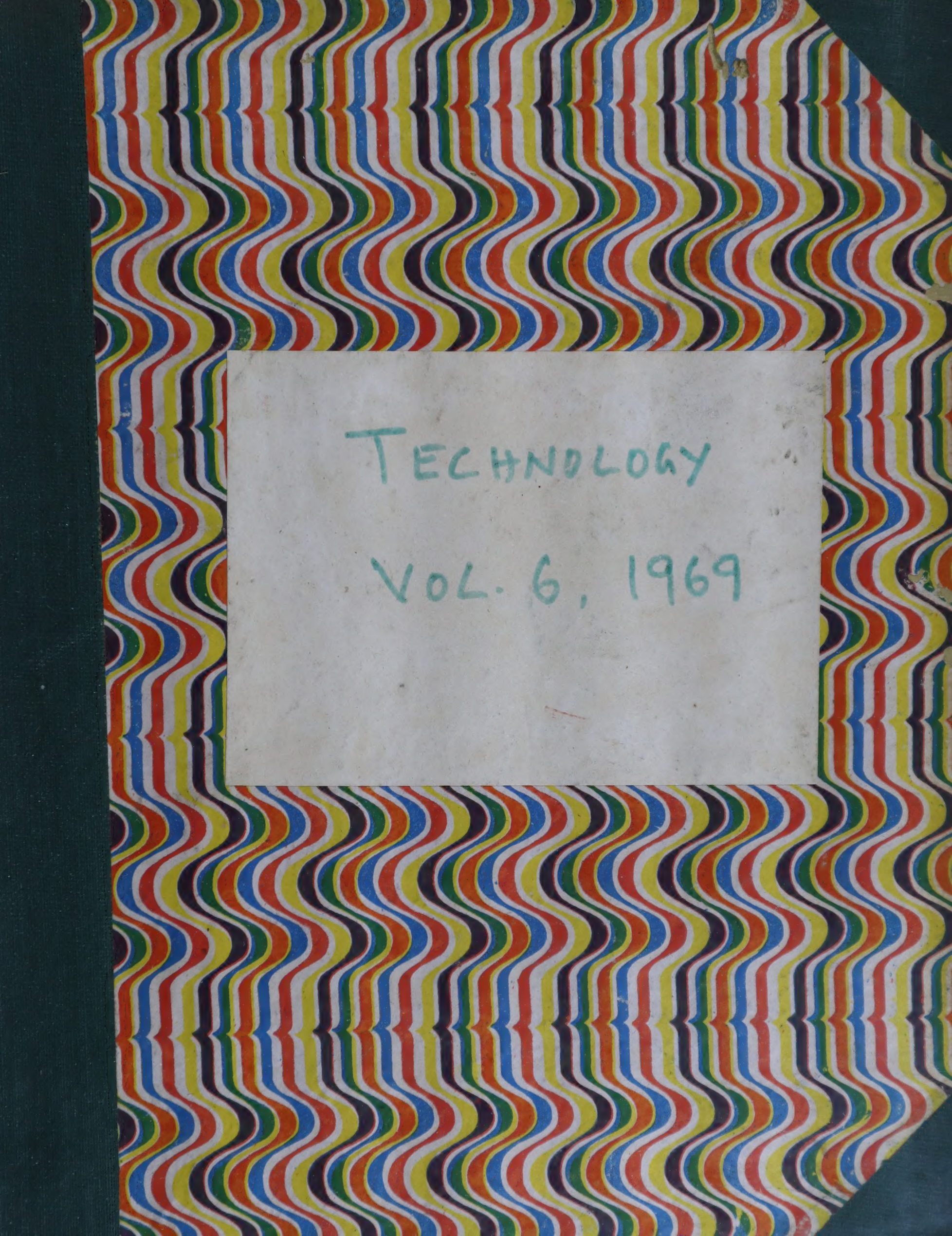
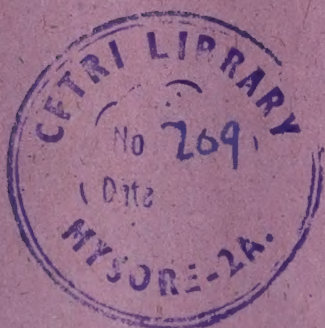




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Infrared absorption studies on a commercial sodium polyphosphate admixed with sodium sulphate—a product being produced in this laboratory—have been carried out. Various absorption bands were characterized and compared with other commercial as well as pure sodium polyphosphates. Absorption spectra of commercial polyphosphate were found to contain all characteristic bands of linear and cyclic metaphosphates as in pure synthetic sodium polyphosphate even with high sodium sulphate contents.

Studies on Commercial Sodium Polyphosphate

Infrared Absorption Spectra of $\text{Na}_2\text{O}-\text{P}_2\text{O}_5$

And $\text{Na}_2\text{O}-\text{P}_2\text{O}_5-\text{SO}_3$ Systems

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In industry, sodium polyphosphate glass or Graham salt with $\text{Na}_2\text{O} : \text{P}_2\text{O}_5 = 1:1$, commercially known as Calgon or sodium hexametaphosphate, has been used as a corrosion inhibitor in cooling towers¹, as a descaling agent for boilers², as deflocculant for various settling slurries³, as a hard surface-cleaning agent⁴ and as water softener^{5,6}. This chemical is usually manufactured by dehydration of pure sodium di-hydrogen phosphate⁷. A process for the manufacture of sodium polyphosphate admixed with sodium sulphate has been developed in this laboratory⁸ using trisodium phosphate de-decahydrate—a by-product in the rare earths factory at Alwaye—as a raw material. The product contains 39-42 per cent sodium polyphosphate (27-29 per cent P_2O_5) and is regularly used as a corrosion inhibitor and a descaling agent in the cooling tower waters in Sindri Fertilizer factory.

For evaluating the quality of the commercial polyphosphates and for effecting improvements in their processes of manufacture, a knowledge of their structure is of great importance, and in this connection infrared studies have proved of considerable help. Infrared investigations of Corbridge and Lowe^{9,10} on dry powdered salts of about 153 phosphorus oxy-acid compounds have shown that they possess absorption bands characteristic of the type of anion present. The absorption frequencies have been found to be largely independent of the positive ion. General absorption band characteristics of

each class of anion have been listed and their possible uses in analysis have been indicated. In other papers^{11,12} methods have been presented for the quantitative analysis of condensed phosphates based upon infrared method which is applicable to any phosphate mixtures in which the individual components give reasonably strong and non-overlapping absorption maxima. Gutsev et al¹³ carried out infrared spectroscopic study of the structure and crystallization of Graham glass. Steger¹⁴ showed the structural differences of trimetaphosphate ion in crystal and in solution, on the basis of spectroscopic investigations. Vibrational infrared spectra of various glassy phosphates of different $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$ ratio have been studied by many workers¹⁵⁻¹⁷.

As the commercial sodium polyphosphate, which is being produced in this laboratory, contains phases like $(\text{NaPO}_3)_n$ and Na_2SO_4 , its infrared spectra have been studied in this paper to ascertain its composition and structure. The spectra have been compared with those of various commercially available polyphosphates.

EXPERIMENTAL

Method

Infrared studies with various polyphosphate samples in the solid phase were carried out by potassium bromide disc technique¹⁸ using the Parkin-Elmer Infrared dual grating spectro-photometer Model 421.

The potassium bromide pellets were prepared by taking about 5 mg. of potassium bromide (G. R. and dried at 400°C) in an agate mortar, loaded in a die evacuated and pressed for 10 min. at 15 tons/sq. in. pressure. The pressure was released, the die rotated at 180°C and again pressed in vacuum for at least 10 min. at 20 tons pressure. The diameter of the pellet was 13 mm. having a thickness of 1 mm. The spectra were recorded in the frequency range of 4000 to 500 cm^{-1} .

Materials

Anhydrous Sodium Sulphate: The absorption spectrum for G.R.E. Merck quality anhydrous sodium sulphate is given in Fig. 1. (curve 1)

Synthetic Sodium Polyphosphate: It was prepared by dehydrating B.D.H. (Analar) sodium dihydrogen orthophosphate in a platinum dish to 700°C. The molten mass, thus obtained, was chilled between cooled stainless steel plates. The glassy phosphate was powdered and infrared spectra recorded Fig. 1 (curve 2).

Fused Mixture of Anhydrous Sodium Sulphate and Synthetic Sodium Polyphosphate: It was prepared by mixing 42 g. of synthetic sodium polyphosphate with 58 g. anhydrous sodium sulphate. The mixture was heated to 900°C and the hot fluid mass was chilled on stainless steel plates. The absorption spectra are given in Fig. 1 (curve 3).

Commercial Polyphosphate I: It is sodium hexameta-phosphate (B.D.H.). Its infrared spectra are presented in Fig. 1 (curve 4).

Commercial Polyphosphate II: It is sodium hexameta-phosphate from M/s Star Chemicals, Bombay. Its absorption spectra are given in Fig. 1 (curve 5).

Commercial Polyphosphates III and IV: These are the samples from two batches of sodium polyphosphate which are being produced in this laboratory by the following process⁸.

Commercial trisodium phosphate dodecahydrate is mixed with ammonium sulphate in a proper ratio. The mixture is heated for 45 min., in an open hearth furnace at 900°C. The hot fluid mass is quenched by pouring on a stainless steel tray kept cool by water. The product is a solid mass which contains 28 per cent total P_2O_5 of which 99 per cent is present as sodium polyphosphate. Samples were powdered and subjected to infrared analysis. The spectra are presented in Fig. 1 (curves 6&7).

The P_2O_5 content of the polyphosphate sample was determined, after hydrolysing with concentrated nitric acid¹⁹, by the standard gravimetric method²⁰. Sulphate

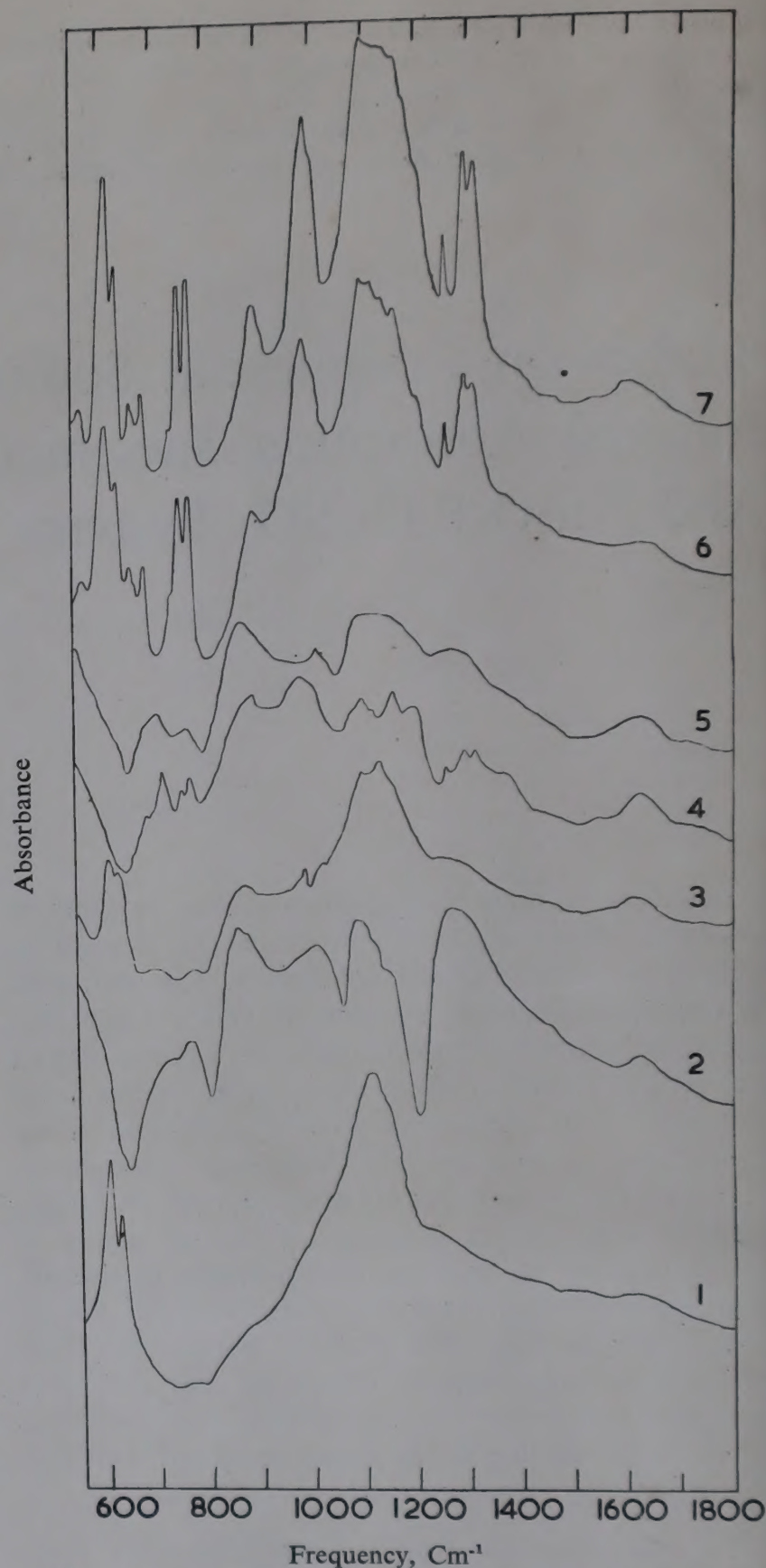


Fig. 1—Infrared Spectra of Sodium Sulphate and Synthetic and Commercial Polyphosphates

- 1—Sodium Sulphate (anhydrous)
- 2—Synthetic Sodium Polyphosphate
- 3—Fused Mixture Sodium Polyphosphate (Synthetic) and Sodium Sulphate (Anhydrous)
- 4—Commercial Polyphosphate I
- 5—Commercial Polyphosphate II
- 6—Commercial Polyphosphate III
- 7—Commercial Polyphosphate IV

content of polyphosphate samples was determined by standard barium chloride method²¹. The end group or

number average molecular weights were determined by pH titration method²². The end group molecular weights and analyses of various polyphosphate samples are given in Table 1.

TABLE 1—ANALYSIS AND NUMBER AVERAGE MOLECULAR WEIGHTS OF SODIUM POLYPHOSPHATE SAMPLE

Sl. No.	Samples	Average Molecular Weight	P ₂ O ₅ , %	SO ₄ , %
1.	Synthetic Sodium Polyphosphate	4,065	69.0	—
2.	Fused Mixture of Sodium Sulphate and Synthetic Sodium Polyphosphate	2,400	29.0	38.54
3.	Commercial Polyphosphate I Sodium Hexametaphosphate from B.D.H.	630	68.9	—
4.	Commercial Polyphosphate II Sodium Hexametaphosphate from Star Chemicals, Bombay	600	57.6	—
5.	Commercial Polyphosphate III (Laboratory Product)	2,670	26.7	39.6
6.	Commercial Polyphosphate IV (Laboratory Product)	2,720	27.0	39.5

Results and Discussion

Infrared spectra of all the commercial polyphosphate samples, together with synthetic polyphosphate, sodium sulphate and fused mixture of latter two materials are produced in Fig. 1 (curves 1-7). The frequencies of the bands and their assignments are presented in Table 2. The assignments have been made after Corbridge and Lowe^{9,10}.

The weak band at 1640-1610 cm⁻¹, which is present in almost all the samples of polyphosphates, is the OH bonding mode of the water of crystallisation in the samples or is due to absorption of moisture during KBr pellet preparation.

The three sharp and strong absorption bands at 1312, 1295 and 1258 cm⁻¹, present in commercial polyphosphates I, II and IV, are due to cyclic metaphosphate present in them (Fig. 1, Curves 4, 6 and 7). In linear metaphosphate the three bands in this region are replaced by a single very strong broad band at 1270 cm⁻¹, which is observed in commercial polyphosphate II, synthetic polyphosphate and fused mixture of sodium sulphate synthetic polyphosphate. This is confirmed by the appearance of a strong broad band at 875-865 cm⁻¹ of linear metaphosphate (Fig. 1, curves 5, 2 and 3). The cyclic nature of commercial polyphosphate samples

I, III and IV is further corroborated by the distinguishing strong band at 992-980 cm⁻¹, present in them along with the appearance of a medium strong sharp doublet at 773 and 754 cm⁻¹ together with another medium intensity doublet at 685 and 662 cm⁻¹ which are characteristics of cyclic metaphosphates (Fig. 1, curves 4, 6 and 7).

The range of 1200—1000 cm⁻¹, is the region of ionic phosphate vibration (P-O stretching) of orthophosphates. The presence of orthophosphate in synthetic sodium polyphosphate, commercial polyphosphates I and II is almost certainly due to a number of strong bands in this region (Fig. 1, curves 2, 4 & 5). However, in commercial polyphosphate III and IV and fused mixture of sodium sulphate and synthetic sod. polyphosphate, the very strong and very broad band of SO₄²⁻ ion at 1120 cm⁻¹ masks this region over the orthophosphate bands and makes the identification of each other difficult. But the other strong doublet of SO₄²⁻ ion at 635 and 613 cm⁻¹ is free from any interference and can decipher the presence or absence of SO₄²⁻ ion. SO₄²⁻ ion is present in fused mixture of sodium sulphate and synthetic polyphosphate and commercial polyphosphates III and IV. Therefore the presence of orthophosphate is certain in synthetic polyphosphate (along with linear metaphosphate but cyclic metaphosphate is absent), commercial polyphosphate I (along with cyclic metaphosphate) and commercial polyphosphate II (along with linear metaphosphate). In commercial polyphosphates III and IV and fused mixture of synthetic polyphosphate & sodium sulphate, due to superimposition of very strong and broad sulphate band at 1000-1200 cm⁻¹ region, it is difficult to assert the presence of orthophosphate. However, close scrutiny shows a number of bands superimposed over the sulphate band in this region indicating the formation of orthophosphates in these two samples also, though may be to a lesser extent than the other varieties of polyphosphates. The band at 895 cm⁻¹ observed in commercial polyphosphate I, III and IV could not be correctly assigned; it may be a characteristic of cyclic metaphosphate.

The band at 718-712 cm⁻¹, which has appeared in commercial polyphosphates I and II and at 735 cm⁻¹ in synthetic polyphosphate, may be due to harmonics of P-O bonding in the phosphates containing P-O-P linkage.

From infrared spectra study of commercial polyphosphate, which is being produced in this laboratory, it can be concluded that the presence of excess sodium sulphate, which is formed as a co-product, does not affect the formation of sodium polyphosphate; sodium sul-

(s—strong, m—medium, sh—shouldered, w—week)

[illegible]

phate remains an inert compound. Infrared spectra of these commercial samples show all the characteristic bands of linear and cyclic phosphates, except no. II which does not contain any cyclic phosphate. The presence of tripolyphosphate, pyro-phosphate, trimetaphosphate and tetrametaphosphate along with long chain phosphate have been detected and can be explained as due to high $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$ ratio (>1); these phosphates also come under the class of polyphosphates²⁴. The absorption spectra of all the polyphosphates studied are independent of chain length, since low molecular weight compounds have also been found to give characteristic absorption bands of chain and cyclic metaphosphates, which are shown by high molecular weight compounds. Shifting of bands have been observed in some cases, which is known to depend on chain length of the polyphosphates⁹.

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An high adsorption capacity silica gel has been developed for hydrocarbon type analysis in petroleum products which can be used in place of the imported Davison Grade 923. The gel has a surface area of $811\text{m}^2/\text{g}$ and pore volume 0.4666 c.c./g . Its other characteristics, with special reference to its adsorption capacity and polymerization tendency, are reported here.

High Adsorption Capacity Silica Gel and Its Characterisation for Analysis of Petroleum Products by Adsorption Chromatography

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Silica gel as an adsorbent has been widely used in hydrocarbon type separation of light-run petroleum fractions and industrially utilized for isolating pure individual components¹. The undesirable catalytic tendency of silica gel is known to change the nature of certain olefins. Thus, whereas it is most desirable that the gel for hydrocarbon-type analysis should possess an high adsorption capacity, for aromatics and olefins it should not effect any structural changes. This property to cause polymerization should either be totally absent or negligible. Since the properties of gel vary with its techniques of preparation which govern its field of application, a method has been developed to prepare silica gel indigenously, hitherto imported as Davison Grade 923. Mair¹ has shown its immense analytical applications for hydrocarbon-type analysis. Fink, Lewis and Weiss² have examined its different characteristics required for petroleum analysis. Davison Grade 923 has been preferred by them because of its high adsorption capacity and low polymerization tendency. The American Society of Testing Materials and the Institute of Petroleum, (London) have tentatively accepted Davison gel in their standard methods of analysis.

Petroleum refineries and fertilizer and petro-chemical industries require quick routine test for the group composition of naphtha and other petroleum fractions. The demand of this gel has been assessed to increase considerably in future. In view of the high cost of the imported gel and to effect import substitution, detailed studies on the various properties of indigenous gels have

been carried out, and a method for preparation of an high adsorption capacity silica gel has been developed by the present authors³. Recently, a similar gel for FIA method has been reported by the Indian Institute of Petroleum⁴, Dehra Dun. In this paper, a comparative study on the laboratory gel with particular reference to its high adsorption capacity, low polymerization tendency and other related properties, has been made.

Experimental

The method of evaluation of laboratory gel is mostly based on the principles proposed by Weiss² et al and this technique utilizes refractive index as an additive property. The capacity of the gel is defined as the amount of aromatics retained from a 20 per cent v/v solution of benzene, toluene or any of its derivatives containing C and H and one benzene ring in its structure in iso-octane that exists in light-run distillates, like naphtha per 100g. of the adsorbent gel. In general, toluene has been taken as a representative of aromatics in preparing the synthetic blends and its concentration has been maintained at 20 per cent v/v, because the light-run distillates of most of the Indian refineries contain aromatics upto or less than this concentration. Iso-octane (BDH), di-isobutylene (2,4,4-trimethyl-1 pentene, Phillips research grade 99.5 mole per cent purity) and cyclohexane (E. Merck chromatographic grade) have been taken as representative constituents of paraffins, olefins and naphthenic groups respectively. In calculating the

adsorption capacity, the equation by Weiss (given below) has been used.

$$V_T \left\{ \frac{1 - 10^4(N-n)}{210} \right\} V_M,$$

where V_T = volume of aromatics adsorbed from the mixture, ml.

V_M = volume of mixture associated with V ml. of aromatics separated from the mixture, ml.

N = Refractive index of the mixture from which aromatics is to be separated.

n = Refractive index of either pure solvent, like iso-octane (1.3195) in binary mixture, or of paraffins-olefin mixture as a solvent.

The experiment was performed in a pyrex glass column 10 mm. I.D. and 400 mm. length at $25 \pm 2^\circ\text{C}$ in an air-conditioned room. The mixture was percolated through the packed column at a very slow rate (2 ml./hr. approx.), and it took nearly 8 hours for one set of experiments. The quantity of gel packed in the column varied from 10 to 12 g. The fractions collected were 0.5 ml. cuts and the refractive indices in all the cases, except polymerization studies were determined by a Pulfrich refractometer* (accuracy upto 0.001 unit). In case of the polymerization study, the refractive index was determined with a high precision Abbe Refractometer Model 60 having an accuracy of 0.00004 unit. Utmost care was taken so that volatilization loss during the experiment was minimum. Each blend was prepared immediately before the actual experiment. The silica gel was activated in each case at $130-150^\circ\text{C}$ for not less than 3 hours and packed in suitable glass containers. The gel was transferred through glass tubes into the column to avoid moisture adsorption from atmosphere while packing in the column. The gels, procured from Messrs Keromos Pvt. Ltd., Calcutta and Messrs Producer's Forum, Calcutta, were exhaustively purified with aqua regia to remove organic matter and then with concentrated hydrochloric acid and washed to pH 6.0. The capacity of the commercial gels doubled approximately on purification. The laboratory gel has been used as such without further purification. A comparative data on adsorption capacity of various silica gels is presented in Table 1.

Results & Discussion

The results (Table 1) indicate that the laboratory gel

*Supplied by M/s. Andhra Scientific Co., Madras.

TABLE 1—ADSORPTION CAPACITY OF SILICA GELS FROM A BINARY MIXTURE OF 20% v/v TOLUENE IN ISO-OCTANE

Name of Supplier	Approximate Size mesh, (BSS)	Adsorption Capacity, ml. toluene/100 g. gel.
1. M/s. Gouri Chemicals, Calcutta	-30+100	9.0
2. M/s. Keromos Pvt. Ltd., Calcutta	-52+80	11.75
3. M/s. British Drug House Ltd., London	-30+80	12.0
4. M/s. Producer's Forum, Calcutta	-30+100	13.6
5. Laboratory gel	Coarser	23.1

possesses much higher adsorption capacity than the available commercial gels. The maximum capacity for Davison grade reported by Weiss et al² is 20 ml./100 g. of the gel.

The separation efficiency of the gel is known to be a function of the particle size of the adsorbent along with other variables, like L/D ratio of the column. The evaluation of the effect of particle size on adsorption capacity was necessitated by the following two facts. Weiss² et al have studied different samples of silica gel in which all fractions contained fine particles upto 200 mesh (B.S.S.), but have given no indication about the relative amounts of varying mesh sizes in the mixture. Secondly, the relative performance of laboratory gel too has to be established on varying the particle size. In this study, an attempt was made to choose as uniform a size of the particle as possible in order to assess the possible size-effect. The sieving was done by a dry method and the fractions indicated in Table 2 were chosen. Each fraction was resieved till the amount of under-size was

TABLE 2—EFFECT OF PARTICLE SIZE ON ADSORPTION CAPACITY OF GEL (20% v/v TOLUENE-ISO-OCTANE MIXTURE)

Source of Gel	Size Studied, mesh (BSS)	Adsorption Capacity, ml. toluene/100 g. adsorbent
1. Laboratory gel	Coarse	23.1
	-30+52	21.1
	-60+80	22.14
	-80+100	22.63
	-100+120	22.77
2. Gouri Chemicals, Calcutta	-30+52	6.8
	-60+80	7.1
	-80+100	7.8
	-100+120	8.9

negligible. Of the two gels selected for this purpose, one was of a high adsorption capacity (laboratory gel) while the other of low capacity (Gouri Chemicals). The sample, in each case, was activated between 130 and 150°C for 3 hours. The smallest size studied was upto 120 mesh (B.S.S.), beyond which it becomes too difficult to maintain the flow rate without applying positive pressure. The data on particle size effect are given in Table 2.

The data on adsorption capacity with size reduction indicate that although there is a slight change in capacity with reduction in size yet the increase cannot be taken as substantial to affect the capacity of the gel. Thus, the general conclusion is in agreement with observations made by Weiss et al². As a matter of fact, size reduction by mechanical grinding increases the surface area substantially but this increase is probably too small as compared to the total surface area of silica gel, which is 811 m²/g. in this case. The increase in adsorption capacity after grinding from 30 to 120 mesh seems to be due to the increased rate of adsorption and not the change in surface area due to grinding. In mechanical grinding, probably the macropores have been destroyed primarily and the heat developed due to grinding action has caused destruction of fine pores also to some extent. The overall effect in maintaining the adsorption capacity almost constant, even though an increase in surface area is expected, appears to be due to the destruction of macropores in mechanical grinding. This observation is also confirmed by Rootare⁵ on the effect of ball mill grinding on the pore structure of coconut shell.

Polymerization Activity of Laboratory Gel: As silica gel is known to cause polymerization⁶ of the olefins and bring the structural changes, it is desired that laboratory gel should be free from this undesirable property. The data on investigation of laboratory gel with particular reference to the effect of activation temperature and residence time and catalytic activity are presented below (Table 3).

The effect of tempering and residence time on polymerization activity of laboratory gel was studied by percolating di-isobutylene through a 12 g. packed silica gel bed adsorption column 10 mm I.D. and 400 mm. length. The di-isobutylene was treated with anhydrous sodium sulphate to remove moisture. The two important parameters, viz. residence time and activation temperatures, were particularly studied by varying one and maintaining the other constant. The gel was found to exhibit optimum adsorption capacity when activated between 130-150°C for 3 hours minimum. The flow rate was maintained at 3.0 ml./hr. The residence time was taken when the first drop from the column emerged out and 0.5 ml. cuts with 10 fractions were collected in each set of experiments.

The results (Table 2) indicate that slight reduction in refractive index takes place when the gel is activated upto 150°C and then an increase in the index value follows at 200°C. for the same residence time. The reduction in index value is attributed to an increase in the per cent purity of 2,4,4 trimethyl-1-pentene due to partial separation of 2,4,4 trimethyl-2-pentene of higher refractive index over silica gel column. This is borne out by the fact that infrared spectra of di-isobutylene before (Fig. 1) and after (Fig. 2) percolation do indicate a reduction in concentration of the component, which is characteristically detected at 1655 cm⁻¹ olefin group range and at frequency 825 cm⁻¹, which is the peak for 2,4,4 trimethyl-2-pentene. The characteristic frequency of 2,4,4, trimethyl-1-pentene is detected at 890 and 1640 cm⁻¹.

The calculation of peak area for impurity 2,4,4 trimethyl-2-pentene indicates a reduction of 8.4 sq. mm. and the nature of peak in the percolation sample at 1650 cm⁻¹ becomes less effective than in the original sample. Though all the peaks are identifiable, they have not been discussed being not related with the nature of work. The di-isobutylene has been tested for non-olefinic impurities by the F.I.A. method with standard olefinic marker before and after percolation over silica gel by A.S.T.M/

TABLE 3—EFFECT OF ACTIVATION TEMPERATURE AND RESIDENCE TIME ON CATALYTIC ACTIVITY OF THE LABORATORY GEL FOR 2,4,4 TRIMETHYL, 1—PENTENE

Sl. No.	Residence Time, hr.	Activation Temp., °C	Refractive Index at 28.5°C	Residence Time, hr.	Activation Temp., °C	Refractive Index at 28.5°C
1.	2.0	28.0	1.40505	1.0	140±2	1.40476
2.	2.0	110±2	1.40478	3.0	140±2	1.40480
3.	2.0	150±2	1.40474	6.0	140±3	1.40554
4.	2.0	200±5	1.40478	9.0	140±5	1.40602

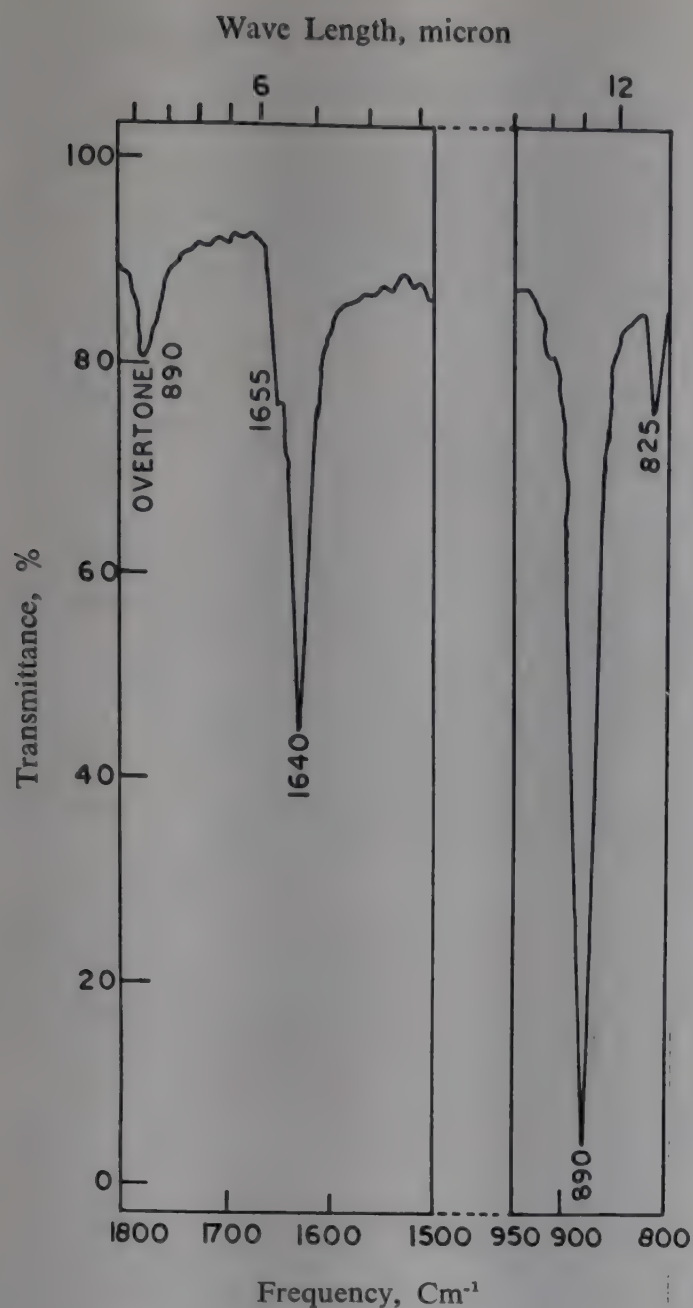


Fig. 1

Sample: 2, 4, 4 Trimethyl-1-Pentene

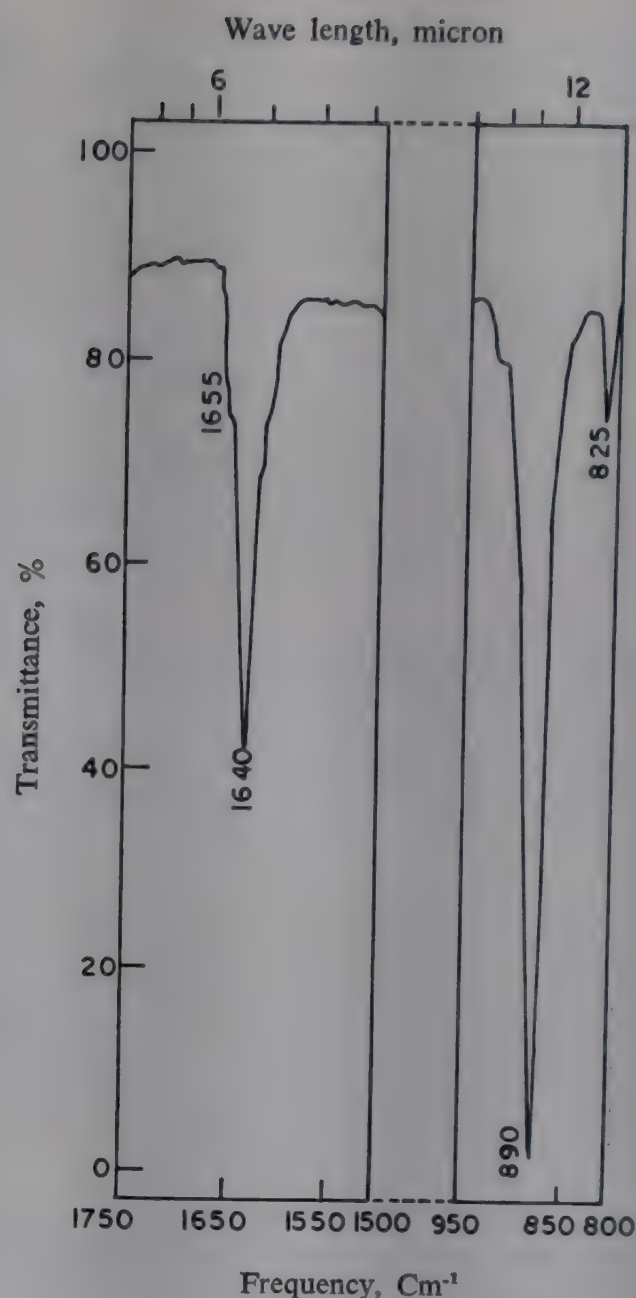


Fig. 2

Sample: 2, 4, 4 Trimethyl-1-Pentene

D/1319-65T, which has given no indication of the presence of foreign substances except olefins. A slight increase in the index value on gel activated at 200°C may be due to the effect of water which increases the catalytic activity as observed by Weiss² et al. They have shown that the tendency of Davison and international gels to polymerize olefins increases when water-loss increases from 0.49 to 0.7 per cent by weight although the capacity remains substantially constant. No specific mention is made as regards the effect of residence time on catalytic activity by the previous workers.

The effect of residence time in establishing catalytic activity of laboratory silica gel is obviously clear. The change seems to be quite insignificant for a contact period of nearly 3 hours beyond which the effect is detectable. A change (an increase) in index value is marked after 6 and 9 hours of contact time (0.07 per cent approx.) over the original value, which can be taken as

negligible for the type of hydrocarbon analysis. Thus, the characteristic study of laboratory gel reveals that it can be used satisfactorily in hydrocarbon-type analysis as well as large scale separation to remove impurities without affecting structural change to an appreciable extent where high degree of purity is desirable.

Effect of Individual Aromatics Present in Gasoline Range on Adsorption Capacity: In order to prove the validity of the assumption that aromatics present in gasoline range behave like toluene molecule as far as the adsorption capacity of gel is concerned, it becomes imperative to determine the individual adsorption capacity of a few aromatic hydrocarbons in iso-octane as a solvent. The determination becomes more desirable where the requirement of silica gel is to be calculated to remove aromatics from stock solution to get aromatic-free paraffins-naphthenes mixtures or where the desired purity of individual hydrocarbons is to be achieved.

Streiff, Mair and Rossini⁷ have shown such applications on a large scale separation from binary mixtures. The adsorption capacities of individual aromatic hydrocarbons on laboratory silica gel (Table 4) indicate that the difference in the adsorption capacity is not more than 10-15 per cent when mixtures are tested. Thus, it seems reasonable to believe that the aromatics present in low range light-run distillates behave as an average toluene molecule when separated over laboratory silica gel. The adsorption capacity has been determined from a 20 per cent v/v aromatic mixture in iso-octane at 25°C, and it is believed that the behaviour of this gel in this respect is very much similar to that of Davison gel.

TABLE 4—INDIVIDUAL ADSORPTION CAPACITY OF AROMATIC HYDROCARBONS ON LABORATORY SILICA GEL

Sl. No.	Aromatic Tested	Aromatics Adsorbed/100 g. of Gel, ml.
1.	Benzene A.R.	21.96
2.	Toluene A.R.	23.20
3.	p.Xylene E, Merck	21.20
4.	Ethyl benzene (BDH)	20.0
5.	n-Butyl benzene (Phillips Research grade)	22.2

Effect of Solvent Composition on Adsorption Capacity in Ternary Mixtures: The effect of solvent composition in ternary mixtures has been investigated. The data regarding adsorption capacity on laboratory gel at 25°C from a solution of 20 per cent v/v aromatics in each case with varying composition on solvents are reported (Table 5). The need for such investigation arises from

the fact that the concentration of various groups, like olefins and aromatics, in saturates exert appreciable influence on the adsorption capacity of silica gel used in hydrocarbon-type analysis. The common representative samples of these groups, like naphthenic compounds, olefins and aromatics, in paraffinic hydrocarbons and their relative effects on adsorption capacity are illustrated in Fig. 3.

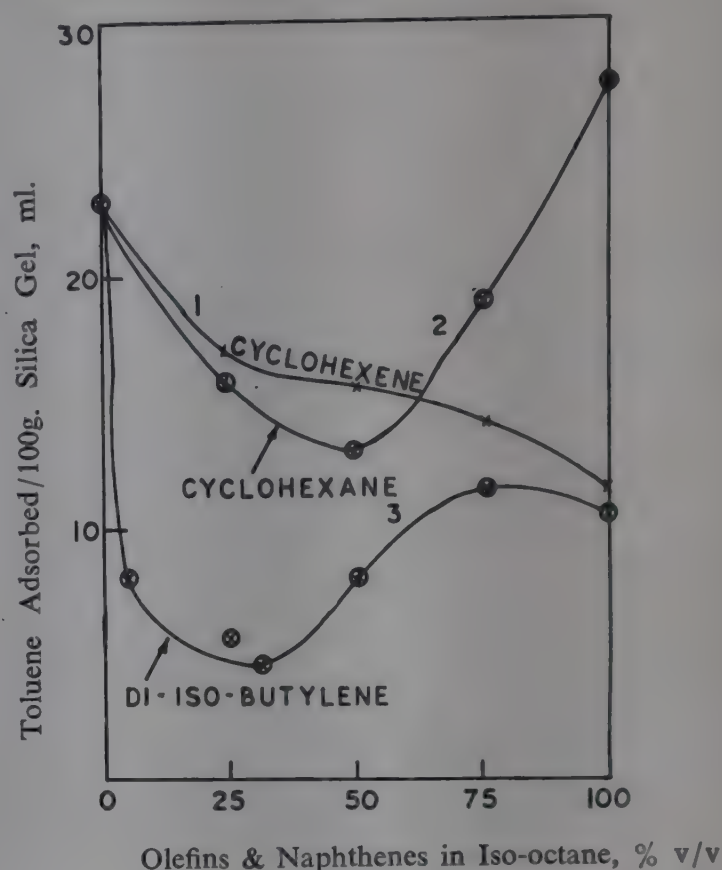


Fig. 3

Legend

1. Toluene—Cyclohexane—iso-octane
2. Toluene—Cyclohexane—iso-octane
3. Toluene—Di-isobutylene—iso-octane

TABLE 5—ADSORPTION CAPACITY OF LABORATORY GEL AT 25°C FROM A SOLUTION OF 20% v/v AROMATICS WITH VARYING COMPOSITION OF SOLVENTS

Sl. No.	Cyclohexane in Iso-octane, %	Toluene Adsorbed 100g. Gel, ml.	Cyclohexane in Iso-octane, %	Toluene Adsorbed 100 g. Gel, ml.	Di-Isobutylene in Iso-octane, %	Toluene Adsorbed 100 g. Gel, ml.
1.	0.0	23.1	0.0	23.1	0.0	23.1
2.	5.0	*	5.0	*	5.0	8.0
3.	25.0	15.8	25.0	17.0	25.0	5.5
4.	31.25	*	31.5	*	31.25	4.4
5.	50.0	13.0	50.0	15.7	50.0	8.0
6.	75.0	19.0	75.0	14.2	75.0	11.6
7.	100.0	27.5	100.0	11.7	100.0	10.4

*These values have not been determined.

The data on adsorption equilibrium for binary solutions only have been reported previously⁸. Our results (Table 5) indicate clearly that adsorption capacity is a function of the selectively adsorbed phase. In case of binary mixtures, the adsorption curve is U-shaped over complete concentration range of olefins from 0 to 100 per cent, while the same is not so simple in ternary mixtures. This indicates that with increasing complexity of the composition such as in naphtha and gasoline, adsorption capacity of gel depends on the relative concentration of the adsorbed phase but does not follow any definite course. The presence of olefins like di-isobutylene reduces appreciably the adsorption capacity and the effect is maximum in the concentration range of 20 to 30 per cent v/v, whereas in case of cyclohexane a sharp fall is observed upto 25 per cent v/v, beyond which the capacity remains almost constant. The effect becomes more pronounced above 80 per cent v/v concentration. The nature of curve deviates appreciably from that observed by Weiss.

The presence of naphthenic constituents, like cyclohexane also reduces the capacity for aromatics, the adsorption being minimum in the vicinity of 50 per cent v/v concentration. In this range, the mixture of paraffinic and naphthenic hydrocarbons is reported to have point of zero selectivity, which explains the reversal in the nature of curves i.e. each component exhibits preferential adsorption depending on the concentration of that particular component in the mixture. The presence of aromatic constituent probably changes the nature greatly and thus an U-shaped curve in place of 'S' type is exhibited⁹. The capacity, thus, seems to depend on the nature and relative concentrations of these groups, which vary widely in magnitude facilitating the separation in hydrocarbon type analysis. By increasing the number of constituents and measuring the adsorption capacities for aromatics and olefins, it may be possible to calculate the quantity of gel required to effect a particular separation. It does not seem to be very sound to consider the behaviour of di-isobutylene as an average olefin in calculating the quantity of gel required without investigating the behaviour of other olefins which exist in petroleum fractions. However, as the presence of olefin in straight-run distillates, such as naphtha, is generally negligible, this gel shows under such conditions high adsorption capacity, which renders it quite suitable for hydrocarbon-type analysis.

Conclusion

The desirable characteristics of a high adsorption capacity gel, developed in this laboratory have been

investigated and compared with those of other commercially available silica gels. The investigations show that this gel is as satisfactory as the imported Davison grade 923 and superior to the other indigenous gels to be used in hydrocarbon-type analysis of petroleum products. It possesses an high adsorption capacity for aromatics and very little polymerization tendency for olefins. It compares favourably with the accepted Davison grade 923 and can be used to substitute the imported gel in the accepted methods of A.S.T.M. and IP (London) for F.I.A. and Refractometry methods of hydrocarbon-type analysis. The specifications of the laboratory gel are given in Table 6.

TABLE 6—PHYSICAL PROPERTIES OF THE GEL DEVELOPED IN THIS LABORATORY

Sl. No.	Specifications of Gel	Experiment Values
1.	Surface area	811 m ² /g.
2.	Pore volume	0.4666 c.c./g.
3.	Average pore diameter	22.9A°
4.	Silica content by HF method	99.89%
5.	Maximum impurity	0.11%
6.	Aromatic adsorption capacity	23.1 ml./100 g.

Acknowledgement

The authors' thanks are due to Dr. B. K. Banerjee, Addl. Superintendent, and Sri A. K. Chakravorty of Physical Research Wing for supplying the infrared data.

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Action of anhydrous magnesium bromide as reaction promoter, along-with ferric oxide as catalyst, for the preparation of 1-naphthyl-acetic acid, in a system containing 0.9 mole of naphthalene and 0.3 mole of chloro-acetic acid was studied. The yield of 21-22 per cent crude product (m.p. 121-125°C) was obtained. It was also found that the addition of potassium chloride in the system enhanced the yield of crude 1-naphthyl-acetic acid to 34 per cent.

Effect of Promoters on Condensation Reaction Of Naphthalene with Chloro-Acetic Acid

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1-Naphthyl-acetic acid of late has found use as a plant growth hormone both for enhancing root development and fruit growth. Generally, it was prepared by the nitrile method¹ via chloromethylation of naphthalene. Since Wolfrom, Schörning and Hausdörfer patented² the formation of 1-naphthyl-acetic acid by the direct substitution of chloro-acetic acid with naphthalene, many workers³⁻⁷ in different countries have studied the same reaction with different catalysts like Fe, FeO, Fe₂O₃, FeCl₃, FeBr₂, FeBr₃, Al and Cr. The different promoters studied were NaCl, NaBr, KCl, KI, CdBr₂, AlCl₃ and HgBr₂. Japanese workers³ investigated the said reaction using ferric oxide as catalyst and potassium bromide as reaction promoter and reported a maximum yield of 34 per cent crude crystallized 1-naphthyl-acetic acid (m.p. 124-126°C) based on chloro-acetic acid used.

Experiments on the same line were conducted in this laboratory using anhydrous magnesium bromide as the reaction promoter. Also, the effect of addition of potassium chloride to the system containing magnesium bromide was studied.

Reagents

The reagents such as chloro-acetic acid, ferric oxide and potassium chloride used in the experiments were of B.D.H. (A.R.) quality. Naphthalene used was of technical grade and anhydrous magnesium bromide used was of E. Merck's G.R. grade. Chloro-acetic acid was dried over concentrated sulphuric acid in a desiccator. Precautions were taken while weighing and transferring the hygroscopic reagents (anhydrous magnesium bromide and chloro-acetic acid) as that practically no absorption of moisture could take place.

Experimental Procedure

Naphthalene (0.9 mole, 115.2 g.) was thoroughly mixed with the catalyst ferric oxide and the reaction promoter anhydrous magnesium bromide. The whole mass was taken in an one litre round-bottomed flask fitted with an air condenser of one meter length and a thermometer dipped into the reaction mass. After the addition of chloro-acetic acid (0.3 mole 28.35 g.) the reaction flask was swirled for some time and then enclosed in a heating mantle equipped with thermostatic temperature control. The temperature was gradually raised to 192-195°C, when the contents of the flask began to boil and the temperature shot up. The reaction time was 24 hours. The effect on yield by prolonging the reaction time to 72 hours was also studied in some cases. After the reaction was over, the contents of the flask were cooled to room temperature and then boiled with 200 ml. of 10 per cent sodium hydroxide solution for about 15 minutes. The whole mass was then cooled to room temperature (28-30°C) and filtered under suction. The residue (excess naphthalene and tarry matter) was washed with a little distilled water and the washings mixed with the filtrate. The filtrate was neutralized with hydrochloric acid and brought to pH 3-4. A white precipitate contaminated with some brownish tarry products was obtained. After filtration the mixed product was taken in distilled water and heated, when most of the tarry matter came out as scum and was left on filter paper. 1-naphthyl-acetic acid that went into solution was crystallized out from the filtrate on cooling. The product was recrystallized from hot water and washed free of adherent salts and dried at 100°C. 1-naphthyl-acetic acid thus obtained was made free from

ny contamination of 2-naphthyl-acetic acid by extracting away the latter with petroleum ether.

Results and Discussion

It was observed that in the absence of the catalyst ferric oxide yield of 1-naphthyl-acetic acid was practically nil and with ferric oxide alone as catalyst and no promoter yield was hardly 5 per cent. Addition of more than 0.15g. of ferric oxide in the system neither hastened the reaction nor improved the yield. No improvement in the yield of 1-naphthyl-acetic acid was found by prolonging the reaction time over 24 hours. The addition of ferric oxide promotes the coupling-reaction⁸ probably by bringing down the activation energy of naphthalene.

The condensation reaction rate was rather slow and required boiling for about 24 hours to attain the equilibrium stage. The boiling temperature which was initially observed to be 195°C rose gradually to 210°C in the course of reaction. There was evolution of hydrogen chloride gas as the reaction proceeded.

Effect of Magnesium Bromide as Promoter: When

potassium bromide (0.84 g.) was added as promoter along with ferric oxide (0.15 g.) as catalyst in the above system the yield of 1-naphthyl-acetic acid, on the basis of chloro-acetic acid used was 30-33 per cent. It was observed that the reaction temperature shot up from 195 to 222°C and remained more or less stationary in the course of reaction. When potassium bromide was replaced by magnesium bromide (0.0035 moles; 0.65 g.) in the same molar proportions as promoter (based on bromine in potassium bromide) the yield of the crystallized crude product (m.p. 121-125°C) was 11-12 g., which corresponded to 20-21 per cent based on the chloro-acetic acid used. Sudden rise and fall in boiling temperature was observed a number of times in the course of reaction. This fluctuation of boiling temperature (198-210°C) was associated with spurt in distillation followed by condensation of the distilled mass at the upper limb of air condenser. The filtrate obtained by alkali extraction was reddish brown and not tarry black as was obtained with potassium bromide. A milky white precipitate, spotted with brownish particles, was obtained on acidification with hydrochloric acid. By varying the quantity of magnesium bromide (Table 1)

TABLE 1—PROMOTER EFFECT OF MAGNESIUM BROMIDE ON THE YIELD
[NAPHTHALENE 115.2 g (0.9 g mole), CHLORO-ACETIC ACID 28.35 g (0.3 mole)
AND FERRIC OXIDE 0.15 g. (0.0009 mole) m.p. OF CRUDE PRODUCT
105-110°C m.p. OF WATER CRYSTALLIZED PRODUCT 120-125°C]

Sl. No.	Magnesium Bromide, g.	Boiling Temperature		Crude Product, g.	Water crystallized product, g.	Yield on the basis of chloro-acetic acid used, %
		Initial, °C	Final, °C			
1.	0.2515 (0.0013 mole)	195	208	12.0	6.0	10.75
2.	0.3524 (0.0019 mole)	196	210	14.0	7.0	12.53
3.	0.4576 (0.0024 mole)	199	212	16.0	9.0	16.11
4.	0.5546 (0.0030 mole)	198	212	17.0	10.0	17.90
5.	0.6543 (0.0035 mole)	198	210	19.0	11.5	20.59
6.	0.7042 (0.0037 mole)	198	210	20.0	12.0	21.48
7.	0.7540 (0.0040 mole)	198	210	20.0	12.0	21.48
8.	0.8675 (0.0047 mole)	198	211	19.0	11.0	19.69
9.	0.9497 (0.0051 mole)	197	212	18.0	9.0	16.11
10.	1.050 (0.0056 mole)	197	213	17.0	8.5	15.21

TABLE 2—PROMOTER EFFECT OF MAGNESIUM BROMIDE AND POTASSIUM CHLORIDE ON THE YIELD. [NAPHTHALENE 115.2 g. (0.9 mole), CHLORO-ACETIC ACID 28.35 g. (0.3 mole) AND FERRIC OXIDE 0.15 g. (0.0009 mole) m.p. OF CRUDE PRODUCT 107—110°C m.p. OF WATER CRYSTALLIZED PRODUCT 120-125°C]

Sl. No.	Magnesium Bromide, g.	Potassium Chloride, g.	Boiling Temperature		Crude Product, g.	Water Crystallized product, g.	Yield on the basis of chloro-acetic acid used, %
			Initial, °C	Final, °C			
1.	0.7042 (0.0037 mole)	0.1142 (0.001 mole)	196	214	21.0	11.0	19.69
2.	0.7032 (0.0037 mole)	0.1436 (0.001 mole)	196	218	22.0	12.0	21.48
3.	0.7040 (0.0037 mole)	0.1835 (0.002 mole)	196	220	23.0	14.0	25.06
4.	0.7038 (0.0037 mole)	0.2278 (0.003 mole)	197	222	24.5	14.0	25.06
5.	0.7035 (0.0037 mole)	0.5016 (0.006 mole)	196	222	25.0	14.5	25.96
6.	0.7044 (0.0037 mole)	0.7118 (0.009 mole)	196	221	26.0	16.0	28.64
7.	0.7042 (0.0037 mole)	0.9238 (0.012 mole)	196	221	27.0	17.5	31.34
8.	0.7038 (0.0037 mole)	1.0543 (0.014 mole)	197	221	28.5	19.0	34.01
9.	0.7040 (0.0037 mole)	1.4952 (0.020 mole)	195	219	25.5	14.0	25.06
10.	0.7042 (0.0037 mole)	2.0418 (0.027 mole)	195	218	25.0	14.0	25.06

added to the reaction mixture, the maximum yield 12g. (21-22 per cent) of crude crystallized 1-naphthyl-acetic acid (m.p. 121-125°C) was obtained with 0.0037 to 0.004 moles of magnesium bromide and 0.15 g. ferric oxide. Results are shown in Table 1.

Joint Effect of Magnesium Bromide and Potassium Chloride: In earlier experiments with potassium bromide as promoter, the boiling temperature of reaction mixture remained more or less stationary at 222°C. Some experiments were also carried out to see the effect of addition of potassium in the system containing magnesium bromide as promoter. Varied amounts of potassium chloride were tried (Table 2). It was found that on addition of (0.014 mole, 1.054 g.) potassium chloride to the system the boiling point of reaction mixture was raised upto 221°C from initial b.p. 195—197°C and fluctuations in boiling temperature were considerably reduced. The maximum yield of crystallized 1-naphthyl-acetic acid

(m.p. 120-125°C) was 19g. which corresponded to 34 per cent on the basis of chloro-acetic acid consumed.

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Differential thermal investigation on some humic acids samples has been performed at subzero temperatures, with particular reference to their structural characteristics. In their cooling curves at different temperatures several endothermic peaks appear, the number of which increases with the increase of humification and the aromatic character of the acids. These peaks have been attributed to the disintegration of the packets of humic acids into smaller units, which is corroborated by an electron diffraction study, indicating that cooling at subzero temperatures enhances their amorphous character. On heating, there is a rebuilding of the packets of the humic acids at the expense of the smaller units but this unification is not so much complete as their disintegration.

Differential Thermal Investigation on Humic Acids at Subzero Temperatures

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Humic acids usually represent a group of closely related substances, primarily in non-nitrogenous form, although in many cases nitrogen is present in their molecules originating, it is believed, from proteins combining with quinones in the main molecules¹. DTA studies reveal that their thermal diagrams are more or less similar to each other indicating a chemical structure essentially of the same type². It is believed that the structural basis of these acids consists of a flat aromatic condensed ring having functional groups like $>C=O$, $-COOH$, phenolic and alcoholic $-OH$ as well as simple aliphatic ethers and hydrocarbon chains. The nitrogen, if present, is in the cyclic and aliphatic forms³, but the extent of aromatization as well as the arrangement of different groups may vary with the soil types⁴. Their molecular and equivalent weights also vary over wide ranges, reported to be within 1000-59000 and 111-345 respectively⁵. They are usually amorphous in nature and their molecules have colloidal dimensions⁶, but they give rise to a few different x-ray diffraction lines⁷, which become more distinct on humification. The 002 band which appears at 3.5 Å in vitrain coal, also appears in its humic acids having the same value for interplanar spacing⁸. A shift of this band to some higher 'd' values indicates an increase of the aliphatic, alicyclic and hydroaromatic materials on the periphery of the aromatic layers of humic acids⁹. Again, the enhanced intensity of the 002 band has been ascribed to the coplanar nature of $-COOH$, $-OH$ and $>C=O$ groups with the aromatic layers, to the decrease in the amount of amorphous material and a small increase in the

number of layers in the packets of humic acids at the expense of those occurring freely¹⁰.

The high temperature DTA curves of the humic acids show exothermic effects in the region 300-600°C. The peaks have been ascribed to the decomposition of their molecules¹¹. So far, there is no information on the transformation of humic acids at subzero temperatures. In the present investigation, attempts have been made to study the differential thermal analysis of some humic acid samples at cryogenic temperatures with particular reference to the role of structural characteristics on their transformations.

Experimental

Humic acids samples taken for the present investigations were the same used previously². They were extracted from the (a) black cotton, (b) Ludhiana, and (c) Chinsura soils and from (d) a ball clay of coal origin. The extraction and purification procedures followed were the same adopted previously². The ash content of the sample (a) is within 2 per cent and the same of the rest is below 1 per cent.

Differential Thermal Analysis: Linseis ultra-low temperature fully automatic DTA instrument was used for this investigation. An iron-constantan thermocouple was used for measuring the temperature differential as well as the temperature of the sample. The sample-holders were made of a non-ferrous metal—one for an inert substance ($\alpha-Al_2O_3$) taken as a standard and the other for the test samples. Purified humic acids samples

oven-dried at 60°C were filled in the sample holder. After adjusting the height of the sample-holders the measuring head containing these was put in a metallic case, which was then inserted in a thermostatic bath containing liquid nitrogen. Gaseous nitrogen was also passed through the chamber containing the probe. The rate of cooling was controlled at 5°C/min. by a programme-controller. The temperature range used was 0 to -120°C. The thermograms were recorded and the heating curve (Fig. 1) of one of the samples was also recorded simultaneously after cooling upto -120°C keeping the rate same (Table 1).

TABLE 1—PEAK TEMPERATURES AND INTENSITY OF THE HUMIC ACIDS SAMPLES

Sample	Peak Temperature, °C			
	Cooling Curves		Heating Curves	
	Endo	Exo	Endo	Exo
1. Black Cotton	-25m, -40m, -60s, -80s, -110w			
2. Chinsura	-30w, -40w, -55m, -80s, -100w			
3. Ludhiana	-55w, -80s, -100w			
4. Ball Clay	-60vw, -75s, -105m			
5. „				-40 to -100mb

s=strong, m=medium, w=weak, mb=medium bulge

X-Ray Diffraction Study: The above oven-dried purified samples used for the DTA study were also used in this study. X-ray diffraction photographs of the samples were taken by a Debye-Scherrer camera (11.5 cm. diam.) in a Philips PW 1010 unit using CuK α radiation generated at 40 KV and 20 mA. The time of exposure was 15 hours in each case. Similar diffraction photographs were also taken for black cotton and Chinsura humic acids after completing the DTA cooling cycle and bringing them at the room temperature. The 002 diffraction band of the humic acids samples ($d_{002} \approx 3.5\text{\AA}$) was microphotometered and the x-ray patterns with the scanning curves are shown in Fig. 2 (a,b).

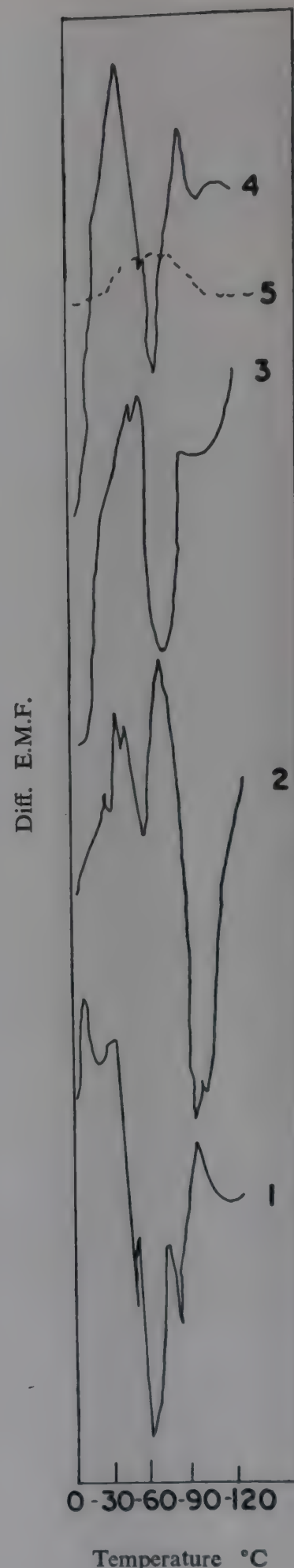


Fig. 1—DTA Thermograms of Humic Acids Samples
Samples: (1) Black Cotton, (2) Chinsura, (3) Ludhiana Soil
(4) Ball Clay, (1-4) represents cooling curve and
(5) heating curve of Ball Clay Samples

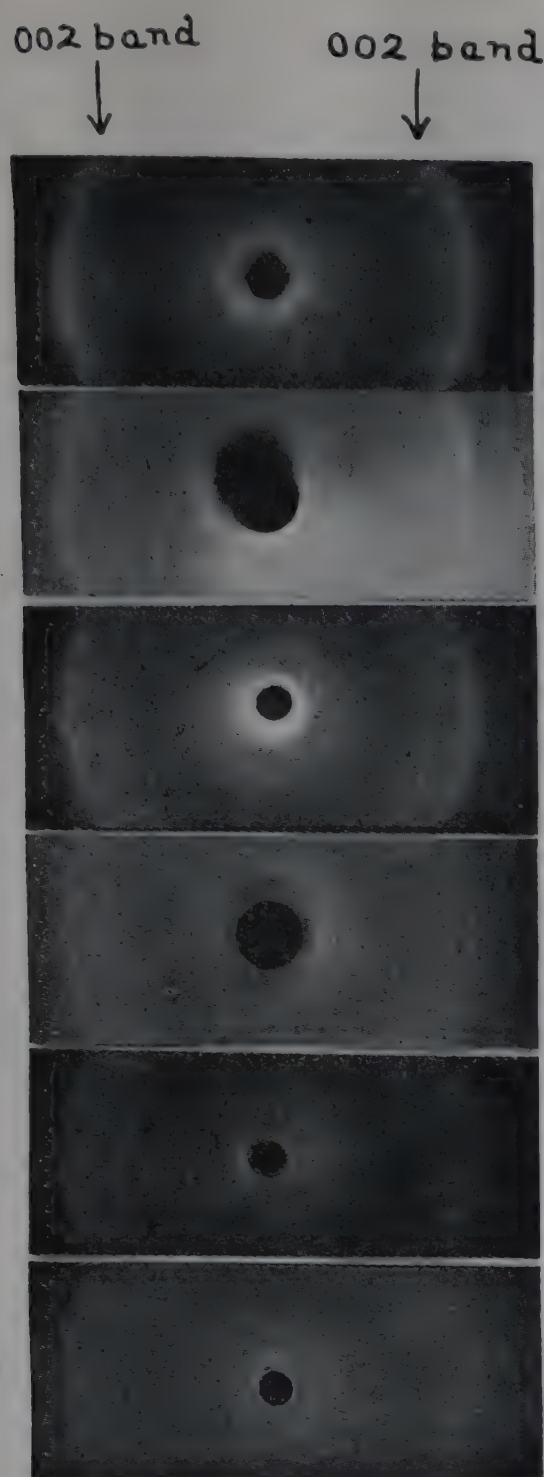


Fig. 2a—X-ray Diffraction Patterns of the Humic Acids Samples

Samples: (1) Black Cotton, (2) Chinsura, (3) Ludhiana Soil (4) Ball Clay samples. 1' and 2' represent samples 1 and 2 cooled to -120°C in the DTA sample holder previously.

Results and Discussion

DTA cooling curves of the humic acids samples reveal several endothermic peaks in the temperature region viz. -25 to -60°C , -75 to -80°C and -100 to -110°C (Fig. 1, Table 1). Of these, the number of peaks in the first zone varies with the samples. Thermal diagram of humic acids extracted from black cotton soil is very similar to that of Chinsura soil humic acids as both of them show three distinct peaks at about -60°C . The intensity of the peaks in the region -60 to -80°C is

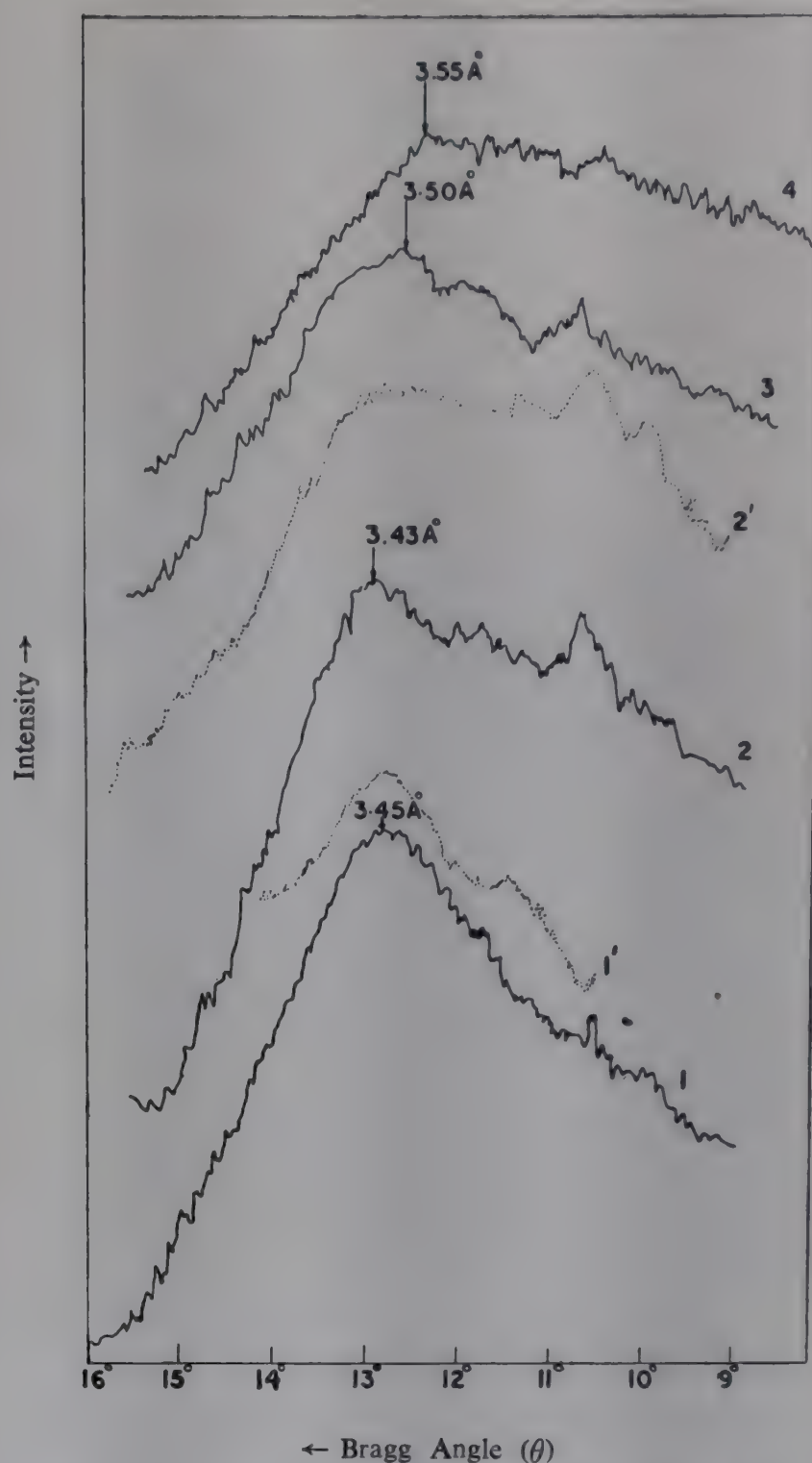


Fig. 2b—Microphotometer Traces of the 002 Band of the Humic Acids Samples

Samples: (1) Black Cotton, (2) Chinsura, (3) Ludhiana Soil (4) Ball Clay samples. 1' and 2' represent samples 1 and 2 cooled to -120°C in the DTA previously.

maximum in each case. It is interesting to mention here that there is also a striking correlation between the DTA observation and the position of the 002 band that appears in the x-ray diffraction patterns (Fig. 2a). In the black cotton and Chinsura samples, the band maximum occurs at 3.45 and 3.43 Å whereas in the Ludhiana and ball clay samples the positions of this band are at 3.50 and 3.55 Å respectively. According to Ergun⁹ et al, the shifting of this band position towards lower 'd' value indicates more humification and enhanced aromatic

character of the samples. It may, therefore, be concluded that the number of peaks increases with enhanced humification and aromatic character of the humic acids. Further, the intensity of the 002 band of black cotton and Chinsura variety is higher than that of the rest (Fig. 2b). It indicates that the functional groups, such as $-\text{COOH}$, $-\text{OH}$ and $>\text{C}=\text{O}$, in the former two cases are more coplanar in their aromatic layer than those of Ludhiana soil and ball clay samples. The enhanced intensity of this band also indicates a small increase in the number of layers in packets of humic acids¹⁰. Consequently, more bondings are involved in the packet formation between the layers of their humic acids, and an increase in the number of peaks in their cooling curves may, therefore, be correlated with these increased bondings.

Usually, diffraction bands of the humic acids become less intense, when the number of their smaller units is large. A preliminary examination of a humic acids sample (from the black cotton soil, having a maximum intensity of 002 band) by electron diffraction shows that the bands that appear at -120°C are not as intense as at room temperature (Figure not shown as the bands are very weak and hardly discernible in the photograph). This indicates that the amorphous character of the sample increases due to cooling at subzero temperatures. It can only be achieved if the packets are disintegrated into smaller units which enhances the amorphous character of the sample. In this connection it may be mentioned that the structure of the other humic acids samples has been found to be similar to that of black cotton variety². It is, therefore, expected that such a cooling procedure will enhance the amorphous character in other cases also. The appearance of the endothermic peaks may, therefore, be ascribed to this disintegration, which is evidently involved in the breaking up of the bonds that hold the layers together in the packets. This has been substantiated by the fact that the intensity of the 002 band of the two humic acids samples (from black cotton and Chinsura soils) is reduced (Fig. 2b). This indicates that the smaller units increase in number due to cooling treatment.

Again, the decomposition temperatures of these bonds are not alike as is evident from the appearance of multiple

peaks in the cooling curves of the samples (Fig. 1, Table 1). This is quite possible because of the fact that the chemical nature and arrangement of functional groups involving in the packet formation of humic acids differ from one another.

There is only one exothermic bulge, extending from about -40 to -100°C , in the heating curve of the humic acids (ball clay variety, Fig. 1). This observation shows that the peaks in the cooling curve are not exactly reversible. The bulge is not also as sharp as the most intense peaks of the cooling curves, and may be due to the rebuilding of packets which takes place progressively during the heating at the expense of those smaller units occurring freely. Further, it is evident from the x-ray diffraction study that there is an increase in the number of smaller units of the humic acids if the samples are cooled previously (Fig. 2a, b). It can therefore, be inferred that the process of unification is not so much complete as disintegration, which is affected by the cooling process.

Acknowledgements

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ammonium nitrate forms with ammonium sulphate double salts having different molar ratios of nitrate-sulphate, containing free ammonium nitrate and ammonium sulphate. It has been shown that the double salt is stable upto 90°C and dissociates into ammonium nitrate and ammonium sulphate at 90°C. At all the temperatures, free ammonium sulphate was found to be present.

X-Ray Study on the Stability of Ammonium Nitrate-Sulphate

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The presence of three double salts of varying molecular composition of ammonium nitrate-sulphate having 1:1, 2:1 and 3:1 molar ratios of nitrate-sulphate was established by x-ray diffraction analysis¹. In our earlier investigation¹ on this system, we have confirmed the existence of 1:1 salt solid phase and further we have studied the crystallographic properties of this salt. The present investigation was undertaken to obtain more information about its thermal stability.

At present, ammonium nitrate-sulphate (1:1) is an established fertilizer. In its manufacture, steps are taken to eliminate from the end-product the free ammonium nitrate, because being sufficiently hygroscopic it creates considerable difficulties in the preservation of the fertilizer. Ammonium nitrate exists at least in 6 crystalline forms³. Of these transitions, the one of the phase, IV $\rightleftharpoons$ III occurs usually around 32°C, but in some cases this takes place between 32 and 55°C depending upon the amount of moisture present in it⁴. Since the normal temperature in this country fluctuates widely around 32°C and sometimes goes even beyond 40°C, the transitions of ammonium nitrate and the fertilizers containing this compound are very much affected in this temperature range. Therefore, it is important to establish clearly whether the compound, ammonium nitrate-sulphate (1:1), is stable or not at these transitions and the conditions under which it is transformed.

Experimental

The x-ray diffraction patterns of the sample of ammonium nitrate-sulphate (1:1) were recorded in an Unicam high temperature powder camera of diameter 19 cm.

with CuK α radiation using nickel filter at the room and high temperatures. Aluminium was used as a standard to calibrate the camera. The time of exposure for each sample was 15 hours. The intensities of lines on x-ray powder photographs for the phase identification was done by the usual method of Hanawalt et al.

The sample was taken in the Lindamen Glass capillary sealed at both ends. The diffraction patterns were recorded under vacuum at different temperatures upto 90°C. The moisture content of the sample was about 1.5 per cent.

Discussion

The present high temperature x-ray study at different temperatures gives a more precise information on the stability of ammonium nitrate-sulphate (1:1). The x-ray diffraction patterns of the double salt were taken in the

TABLE 1

Temperature, °C	Phases Present
Room	1:1 salt, (NH ₄) ₂ SO ₄ , NH ₄ NO ₃ IV
30 and 40	1:1 salt, (NH ₄) ₂ SO ₄ , NH ₄ NO ₃ IV
50	1:1 salt, (NH ₄) ₂ SO ₄
60 and 70	1:1 salt, (NH ₄) ₂ SO ₄
80	(NH ₄) ₂ SO ₄ , NH ₄ NO ₃ III, 1:1 salt
90	(NH ₄) ₂ SO ₄ , NH ₄ NO ₃ II, NH ₄ NO ₂ III

TABLE 2—X-RAY DIFFRACTION DATA OF THE AMMONIUM NITRATE-SULPHATE (1:1) AT DIFFERENT TEMPERATURES

Sl. No.	30 and 40°C		50°C		60 and 70°C		80°C		90°C		1:1 Salt		(NH ₄) ₂ SO ₄		(NH ₄)NO ₃ II		NH ₄ NO ₃ III		NH ₄ NO ₃ IV	
	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I
1.	5.205	15	5.20	25	5.20	25	5.21	35	5.20	10			5.22	27	5.20	30	5.24	17	4.95	45
2.	4.835	40	4.84	15	4.835	15	4.84	5			4.83	90								
3.	4.705	35	4.700	15	4.701	15	4.70	5	4.518	15	4.70	75					4.50	19		
4.													4.39	63						
5.													4.33	100	4.12	70				
6.	4.360	60	4.360	100	4.360	100	4.360	100	4.360	100										
7.									4.127	40										
8.	3.95	15	3.90	35	3.90	25	3.91	20	3.90	30	3.90	15	3.89	35			3.91	53	3.96	67
9.							3.894	15			3.43	20								
10.																				
11.																				
12.							3.384	15	3.398	45							3.39	52		
13.	3.285	100	3.282	50	3.28	35	3.285	10			3.28	100								
14.							2.235	50	3.23	75							3.23	100		
15.							3.17	30	3.170	75	3.18	90			3.17	100	3.20	63		
16.	3.18	50	3.175	40	3.175	40	3.140	15	3.140	25			3.139	20						
17.													3.122	22						
18.	3.07	30	3.065	40	3.065	45	3.06	30	3.06	50			3.055	54					3.09	100
19.	2.915	25	2.91	10	2.91	15		15			2.90	50	3.00	23	2.89	60	2.93	17		
20.							2.85										2.83	34		
21.																			2.722	75
22.	2.74	20						15	2.57	20	2.64	20	2.655	13	2.59	35	2.61	72		
23.	2.643	10	2.64	15	2.635	10	2.622	15												
24.																				
25.	2.437	20	2.44	20	2.435	15	2.415	10			2.44	20					2.41	45		
26.	2.329	20	2.53	25	2.323	20	2.325	25	2.31	25			2.322	17	2.29	30	2.32	19		
27.	2.257	15									2.22	15					2.26	22	2.26	44
28.	2.184	10	2.178	15	2.18	15	2.18	15					2.168	14						
29.	2.125	15									2.12	10								

ange 30 to 90°C. (Fig. 1). 1:1 double salt was found stable upto 70°C, stability decreasing with the rise of

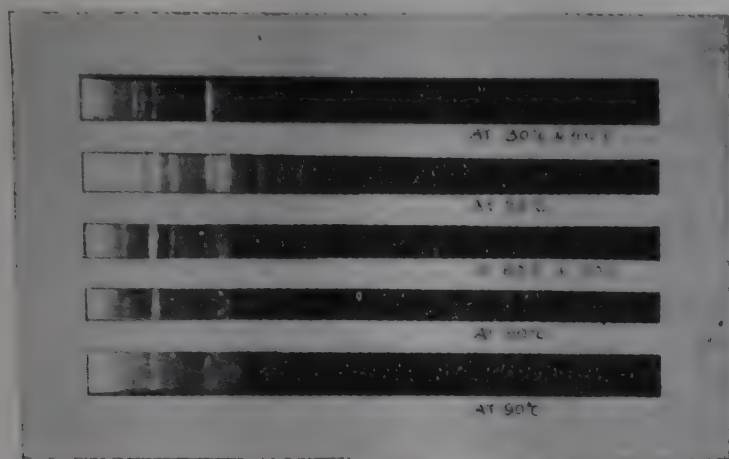


Fig. 1—X-Ray Diffraction Photographs of Ammonium Nitrate-Sulphate at Different Temperatures.

temperature and at 90°C dissociating into ammonium sulphate and ammonium nitrate. The phases present at different temperatures are given below (Table 1).

Curiously enough, the presence of ammonium nitrate in the form $IV \rightleftharpoons III$ above 32°C is a subject of much technological importance, because a number of papers have been published on the shifting of transition temperature of ammonium nitrate above 32°C with different additives. Till very recently, it was an accepted fact that the stability on the higher range of temperature enhanced only to a small extent. But the recent paper of Brown⁵ et al has shown that the stability range of ammonium nitrate form IV can be raised as high as 43.5°C by the addition of very small amounts of ammonium phosphate, ammonium sulphate and boric acid. The ammonium sulphate is as low as 0.01 per cent. Further, they have also stated that by the addition of ammonium sulphate, ammonium phosphate and boric acid, the next transition takes place only at 122-123.5°C, while for II the transformation in pure and dry state corresponds to 84°C. But in the present investigation, it has been observed that ammonium nitrate which is one of the disintegrated products of the double salt at 80

and 90°C, corresponds to forms III and II respectively. DTA study⁶ of the desiccated sample of the double salt has revealed the fact that the peak due to phase $IV \rightleftharpoons II$ transition of ammonium nitrate is absent, whereas at 84°C the peak due to phase $III \rightleftharpoons II$ transition of ammonium nitrate is present. Thus, the authors conclude that the samples dissociate below 84°C. But in the present study, the existence of ammonium nitrate in the form III around 80°C is closely related to the stability temperature of the double salt, ammonium nitrate-sulphate, which is found to be about 70°C. The characterization of ammonium nitrate just after the dissociation of the double salt above 70°C has been found to be ammonium nitrate III, and this phase exists upto 84°C; beyond this temperature, i.e. at 90°C, it is transformed into type II. Incidentally, 84°C represents the transition temperature of form $III \rightleftharpoons II$.

Another significant observation, which requires critical analysis, is that the minor quantity of ammonium nitrate IV, which was present previously along with the double salt upto 40°C as revealed in the x-ray photograph (Table 2), was not detected at high temperature zone between 50 and 70°C. One possibility of the absence of ammonium nitrate can be attributed to the formation of the double salt over this range of temperature with the free ammonium sulphate, which is already present in the system.

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Phosphorus availability and uptake by Sindri red soil, treated with water-soluble, citrate-soluble and citrate-insoluble phosphatic fertilizers has been studied. *Aman* paddy under waterlogged condition was grown in pots and it was found that ammonium phosphate gave higher yield and uptake followed by nitrophosphate, triple superphosphate, superphosphate and least by rock phosphate. In case of Barley crop grown on the same soil it was observed that nitrophosphate gives better result as a residual effect which is followed by superphosphate and triple superphosphate and the least by ammonium phosphate. A critical scrutiny of the results shows that citrate-soluble phosphate gives better results on higher doses of application and supplies phosphates to plants for a longer period. This may be due to the increase in available phosphate at higher doses of application and also releasing the P_2O_5 slowly.

The Availability & Uptake of Phosphorus by Rice & Barley from Phosphatic Fertilizers In the Red Soil of Sindri

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Phosphatic fertilizers manufactured from different processes contain varying amounts of water-soluble, citrate-soluble and citrate-insoluble phosphates. The presence of each of these phases has got a direct relation ship with the availability of phosphates to plants¹.

An earlier study² on the behaviour of water-soluble phosphatic fertilizer with various Indian soils has revealed that the phosphate fixing power of Sindri red soil is highest and quickest amongst all the soils studied. Further, it was also studied³ that a phosphatic fertilizer having both equivalent amounts of citrate-soluble and water-soluble components gave better availability and uptake compared to 100 per cent water-soluble phosphates.

In view of the peculiar nature of Sindri red soil which has been investigated earlier, a study was undertaken to see the relative efficiency and the economical dose of various phosphatic fertilizers obtained from different processes, and also to determine the suitability of finely grounded rock phosphate and nitro-phosphate (carbo-nitric process) as compared to the other phosphatic fertilizers involving sulphuric acid in its manufacture.

Materials & Method

Pot experiments were conducted to compare the efficiency of superphosphate (single), superphosphate (triple), ammonium phosphate, rock phosphate and nitrophosphate (French variety, carbonitric process).

The first three phosphatic fertilizers involve the use of sulphuric acid during their manufacture while the last two do not require the use of sulphuric acid.

Each of the above fertilizers was added to the Sindri red soil at the rate of 0, 45, 90 and 180 kg. of P_2O_5 /hectare. Nitrogen and potash (K_2O) were added uniformly at the rate of 160 kg. of nitrogen per hectare and 45 kg. of K_2O /hectare from ammonium nitrate and potassium chloride respectively. The fertilizers were applied to 10 kg. portions of Sindri red soil (Table 1). The test crop grown was BR-498-2(A) variety *Aman* paddy under waterlogged condition in the year 1965. The barley (BR-22) was taken as a subsequent crop to study the residual effect. All the treatments were triplicated with the pots arranged in a randomised block design. The pots were kept under proper moisture condition. The crops were harvested after 120 days (harvesting time) near the surface of the soil. The fodder and grains in paddy were separated and dried in an oven at 70°C and weighed. The whole barley plant was dried and weighed as above. About 1 g. of the ground material was digested with triacid mixture and the P_2O_5 content in the aliquot was estimated colorimetrically⁴. The available phosphate before and after each experiment was determined according to Bray and Kurtz⁴ and Olsen⁴ et al.

Results & Discussions

The yield and uptake data of paddy as well as barley

TABLE 1—MEAN YIELD OF PADDY STRAW, g./pot

Level of P ₂ O ₅	Rock Phosphate	Super- phosphate	Super- phosphate Triple	Nitro- phosphate	Ammonium Phosphate	Mean
5 kg./hectare	3.83	21.50	23.33	22.33	25.67	19.33
10 kg./hectare	4.30	29.43	33.00	35.33	38.33	28.08
180 kg./hectare	3.53	39.00	38.00	37.33	49.00	33.37
Mean	3.89	29.98	31.44	31.66	37.67	26.93
C.D. of the F mean at 5% level = 8.55						
C.D. of the level mean at 5% level = 6.93						
C.D. of the marginal mean table at 5% level 3.672						

crop are presented in Figs. 1 (a & b) and 2 (a & b). The available phosphates in soil before and after each experiment with both paddy and barley are presented in Table 2.

From the mean Tables 1 and 3, it can be seen that the yields of paddy (straw+grain) at different fertilizer application are highly significant at 5 per cent level. A closer scrutiny of the data reveals that ammonium phosphate gives highest straw and grain yield compared

to other fertilizers and the next followed by nitrophosphate, superphosphate, triple superphosphate and the least by rock phosphate.

Again, comparing the levels it can be seen that the highest level gives the highest yield of straw and grain, which is highly significant at 5 per cent level.

The behaviour of fertilizers at different levels shows that a dose of 90 kg/ hectare of ammonium phosphate gives an yield equivalent to the yields of nitrophosphate,

TABLE 2—AVAILABLE PHOSPHATES IN TREATED SOILS EXTRACTED BY VARIOUS METHODS

Sl. No.			Bray and Kurtz No. 1	Bray and Kurtz No. 2	Olesen's method	Bray and Kurtz No. 1	Olesen's method
			Available phosphate as 'P' ppm. in soil before planting Barley	Available phosphate as 'P' ppm. in soil before planting Barley	Available phosphate 'P' ppm. in soil before planting Barley	After harvesting Barley	After harvesting Barley
1.	Rock phosphate	45 kg./hectare	Trace	12.14	Trace	Trace	Trace
2.	-do-	90 "	Trace	12.10	Trace	Trace	Trace
3.	-do-	180 "	Trace	32.72	Trace	Trace	Trace
4.	Superphosphate	45 kg./hectare	Trace	3.33	Trace	Trace	Trace
5.	-do-	90 "	2.14	5.71	Trace	Trace	Trace
6.	-do-	180 "	4.29	8.10	1.00	Trace	Trace
7.	Triple Superphosphate	45 kg./hectare	Trace	2.38	Trace	Trace	Trace
8.	-do-	90 "	2.14	6.55	Trace	Trace	Trace
9.	-do-	180 "	4.87	7.62	0.30	Trace	Trace
10.	Nitrophosphate	45 kg./hectare	1.43	5.78	Trace	Trace	Trace
11.	-do-	90 "	3.50	12.00	Trace	Trace	Trace
12.	-do-	180 "	5.71	22.63	1.00	Trace	Trace
13.	Ammonium Phosphate	45 kg./hectare	Trace	2.86	Trace	Trace	Trace
14.	-do-	90 kg./hectare	0.71	2.86	Trace	Trace	Trace
15.	-do-	180 kg./hectare	2.14	3.57	Trace	Trace	Trace
Control			Trace	2.14	Trace	Trace	Trace
Original soil			Trace	2.14	Trace	Trace	Trace

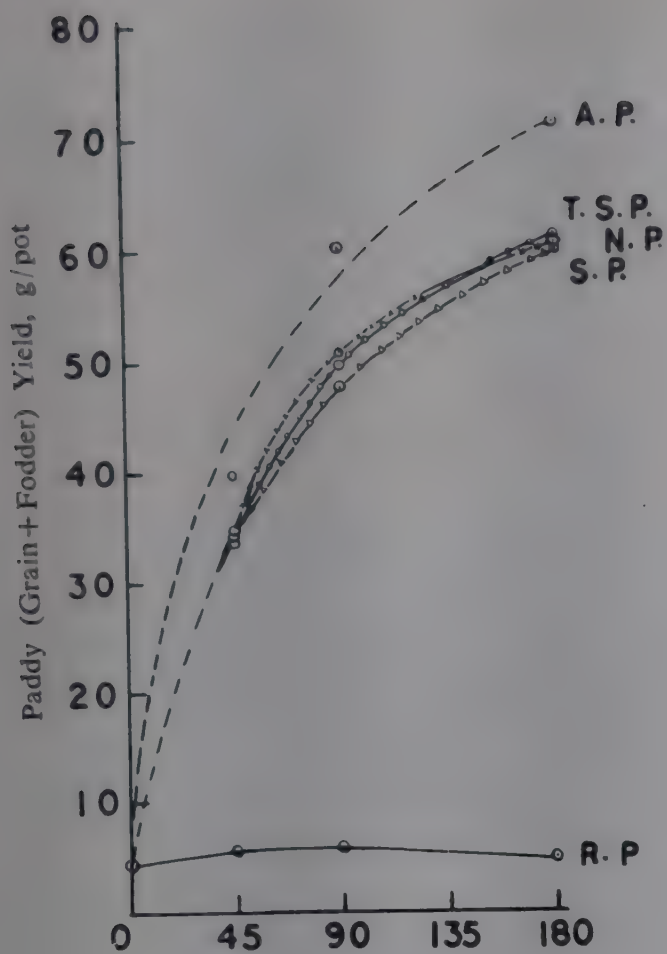


Fig. 1a

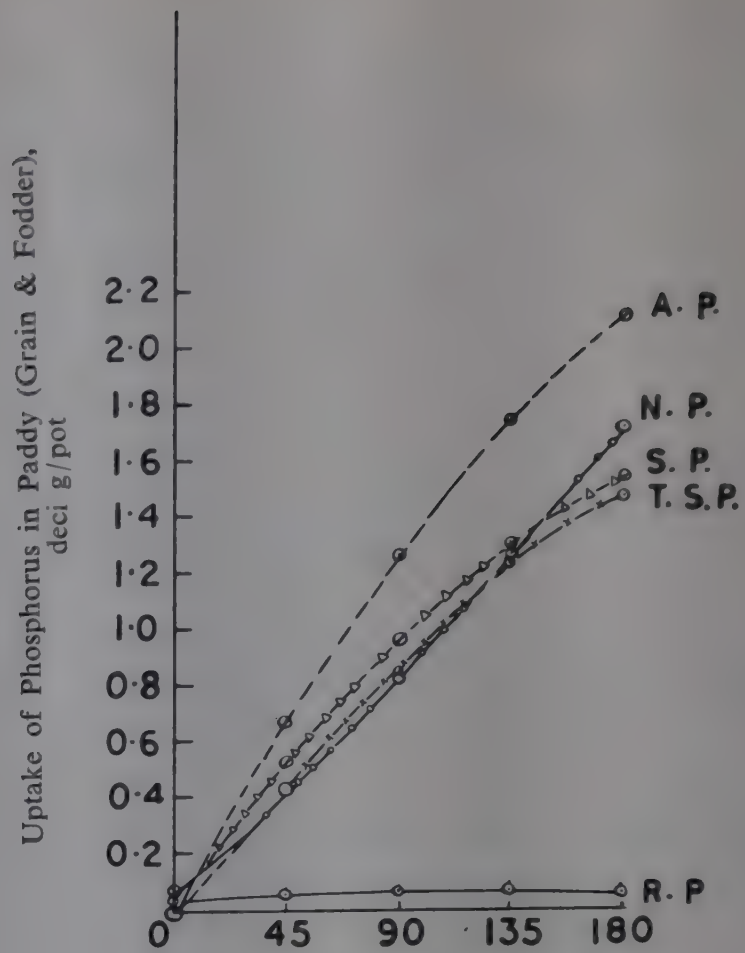


Fig. 1b

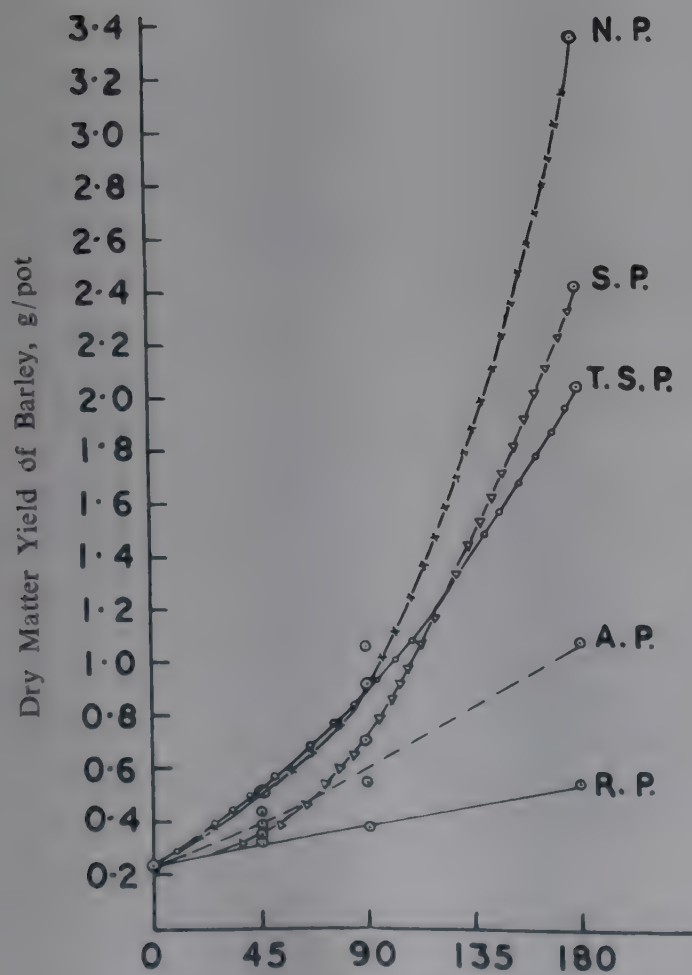


Fig. 2a

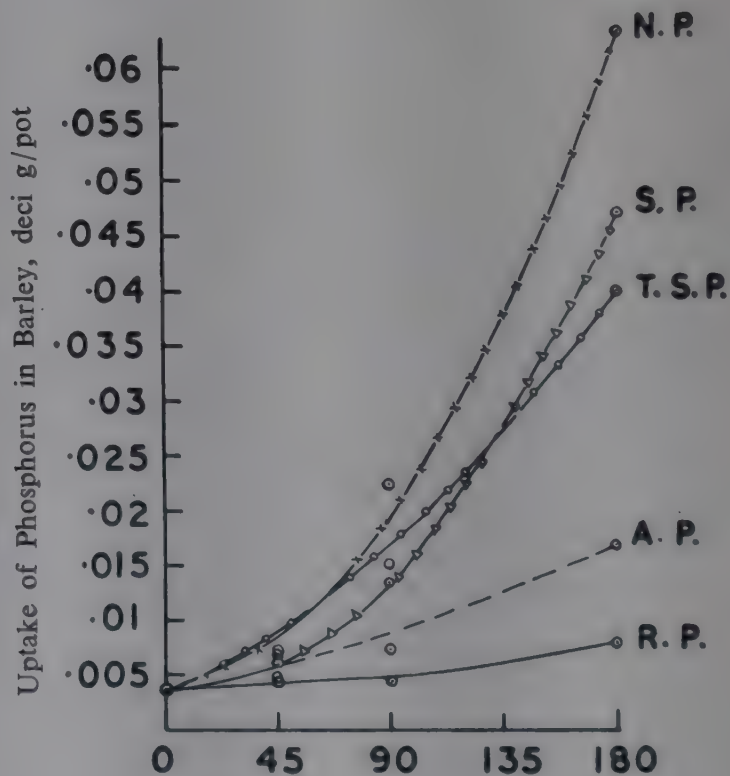


Fig. 2b

TABLE 3—MEAN YIELD OF PADDY GRAIN, g./pot

Level of P_2O_5	Rock Phosphate	Super- phosphate	Super- phosphate Triple	Nitro- phosphate	Ammonium Phosphate	Mean
5 kg./hectare	1.23	12.67	10.33	12.67	14.33	10.25
90 kg./ hectare	1.63	18.33	16.67	15.33	22.00	14.80
180 kg./ hectare	1.40	20.67	23.00	26.33	22.00	18.68
Mean	1.42	17.22	16.67	18.11	19.44	14.58

C.D. of the F means at 5% level = 6.00

C.D. of the level means at 5% level = 4.62

C.D. of the marginal means table at 5% level = 4.90

superphosphate, triple superphosphate at the highest level of P_2O_5 application i.e. 180 kg./hectare. The yield of grain obtained on ammonium phosphate application at the highest level is the same as that obtained at an application of 90 kg/hectare. Different levels of rock phosphate have got no effect on the yield of paddy (grain+straw).

Residual effects of different fertilizers were found non-significant in subsequent barley crop. However, the interaction effects between levels of fertilizers were found to be significant at 5 per cent level. From the mean Table 4 it can be seen that nitrophosphate at 180 kg-Hectare showed the highest yield of barley crop and the next in order were superphosphate and triple superphosphate at the same level of application.

A correlation study was made between yield and uptake of paddy grain, paddy fodder and barley crop. 'r' values were found to be 0.87, 0.96 and 0.99 respectively which were found to be significant at 1 per cent level. Figs. 1 and 2 indicate that as the uptake of P_2O_5 increases, there is a corresponding increase in yield.

Sindri soil is a high phosphate fixing soil and is deficient

in available phosphates (Table 5). It has been studied by Davis⁵⁻⁶ that Bihar soils give very high yield with the P_2O_5 application than K_2O and other fertilizer due to the phosphate depletion in soils. In this study also it was observed the same i.e. very poor paddy yield (grain+straw) as seen from control data, which may be due to the heavy doses of nitrogen without P_2O_5 , and as the P_2O_5 application starts, there is a corresponding increase in yield.

From the available phosphates data (Table 2) it can be seen that the Bray and Kurtz's No. 1 method of extraction of available P_2O_5 from soils has shown the presence of available phosphates in almost all phosphate treated soils and in all levels of application with the exception of rock phosphate treated soil, which shows only traces of available phosphate. The highest available phosphate is shown in soils treated with nitrophosphate followed by superphosphate and triple superphosphate, while ammonium phosphate gave the lowest. The soil treated with higher dose of P_2O_5 has shown higher available phosphates. Bray and Kurtz's No. 2 method of extraction of available phosphates has given high available

TABLE 4—MEAN DRY MATTER YIELD OF BARLEY AS A RESIDUAL CROP, g./pot

Level of P_2O_5	Rock Phosphate	Super- phosphate	Super- phosphate Triple	Nitro- phosphate	Ammonium Phosphate	Mean
45 kg./hectare	0.34	0.36	0.38	0.51	0.43	0.40
90 kg./hectare	0.37	0.70	1.06	0.92	0.54	0.72
180 kg./hectare	0.53	2.42	2.04	3.34	1.08	1.88
Mean	0.41	1.16	1.16	1.59	0.68	1.00

C.D. of the F means at 5% level = 3.696

C.D. of the mean table at 5% level = 0.3302

C.D. of the marginal mean at 5% level = 0.782

TABLE 5—PHYSICO-CHEMICAL PROPERTIES OF SINDRI RED SOIL

Clay Minerals Present	Illite, mainly Kaolinite and Montmorillonite present
Sand, %	58.0
Silt, %	5.0
Clay, %	29.0
C. E. c.m.e./100 g. soil	12.6
Exchangeable Potassium m.e./100 g. soil	1.53
Organic Carbon, %	0.37
Total Nitrogen, %	0.04
Total HCl Insoluble, %	77.65
Total Fe ₂ O ₃ , %	5.27
Total Al ₂ O ₃ , %	7.11
pH	6.6

phosphate in almost all phosphatic treated soils, the highest being given in case of rock phosphate and nitrophosphate followed by superphosphate and triple superphosphate, and the lowest is given by ammonium phosphate. In this case also the available phosphates increased as the level of application were increased. Olsen's method of extraction of available phosphates has shown the presence of available phosphates only in soils treated with highest level of nitrophosphate, superphosphate and triple superphosphate. Triple superphosphate, showed the lowest amount of available phosphate. After the barley crop was taken, the treated soils show only traces of available P₂O₅ indicating that almost all the P₂O₅ was shared by the crop and phosphate fixing minerals present in soils.

Bray and Kurtz No. 2 method has extracted probably the citrate insoluble phosphates, i.e. mostly tricalcium phosphate along with citrate soluble and water soluble phosphates as is observed by the presence of highest available phosphate, in rock phosphate, which is nothing but mostly tricalcium phosphate.

Comparing the data for yield and uptake of barley

with available phosphate (Table 2) present in soil it is clear that some of the citrate insoluble phosphates were available to the barley crop, thus showing higher amounts of P₂O₅ uptake. From the other two methods (Bray and Kurtz No. 1 and Olsen's method) it is clear that with the increased level of P₂O₅ application, the available phosphates also increased and correspondingly the yield of barley also increased. A critical analysis of the results shows that those fertilizers having high water soluble phosphates gave higher yields in the first crop, as because they are quickly solubilised and taken up by plants, but later insolubilised by phosphate fixing constituents present in the soil², thus giving a poor residual effect than those having less water soluble phosphates or, even complete citrate soluble phosphates. The significant point, in case of citrate soluble phosphate, is that it gives better results only at higher levels of application.

The grain yield data were further statistically analysed in order to get an idea about the level of application of P₂O₅ at which maximum grain yield can be obtained. The statistical analysis of the results are enumerated below.

Statistical Analysis

(a) Paddy Grain

Design: The layout of the experimental results has been treated as complete randomised design. As per layout of the design, single level for all of the treatments corresponds to 40 kg. of P₂O₅ per hectare of fertilizer dose; double level corresponds to 80 lbs. P₂O₅ per ha. and the third level corresponds to a dose of 180 kg. of P₂O₅ per hectare.

Findings

The mean yield of grain was obtained by averaging over replications for different levels of doses of fertilizers used in this experiment (Table 6).

Table 7 presents the calculated optimum dose of a

TABLE 6

	Control	Rock Phosphate			Single Superphosphate			Nitrophosphate			Triple Superphosphate			Ammonium Phosphate		
		45 kg./ha	90 kg./ha	180 kg./ha	45 kg./ha	90 kg./ha	180 kg./ha	45 kg./ha	90 kg./ha	180 kg./ha	45 kg./ha	90 kg./ha	180 kg./ha	45 kg./ha	90 kg./ha	180 kg./ha
Mean yield of grains/pot, g.	0.60	1.23	1.63	14.0	12.66	18.33	20.66	10.30	16.60	23.00	12.60	15.30	23.00	14.33	22.00	22.00

TABLE 7

Sl. No.	Rock Phosphate	Single Super-phosphate	Nitrophosphate	Triple Super-phosphate	Ammonium Phosphate
1. Maximum mean yield (estimated), g./pot	1.70	22.00	22.70	23.00	25.00
2. Optimum level of dose (estimated) in kg./ha	118.80	144.00	187.00	189.00	135.00

fertilizer and corresponding expected yield of grain separately for five different treatments.

A joint inspection of Tables 6 and 7 will give an idea about the performance of five different fertilizers and their relative order of performance in producing better yields of grain.

Evidently, the ammonium phosphate comes first in order of merit. An amount of 25 g. of grain yield is expected from an optimum dose of 135 kg/hectare of this fertilizer. This is followed by nitrophosphate, triple-superphosphate, single superphosphate and finally the last place is occupied by rock phosphate.

In these cases of fertilizers, a quadratic response in yield of grain is strongly suspected within the range of doses tried. Five response curves for five different fertilizers are presented in Fig. 3 (a-e).

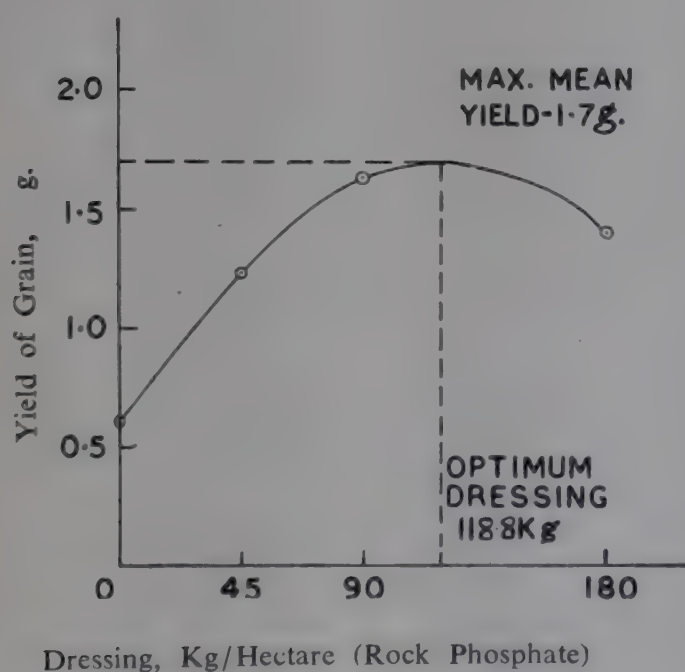


Fig. 3a

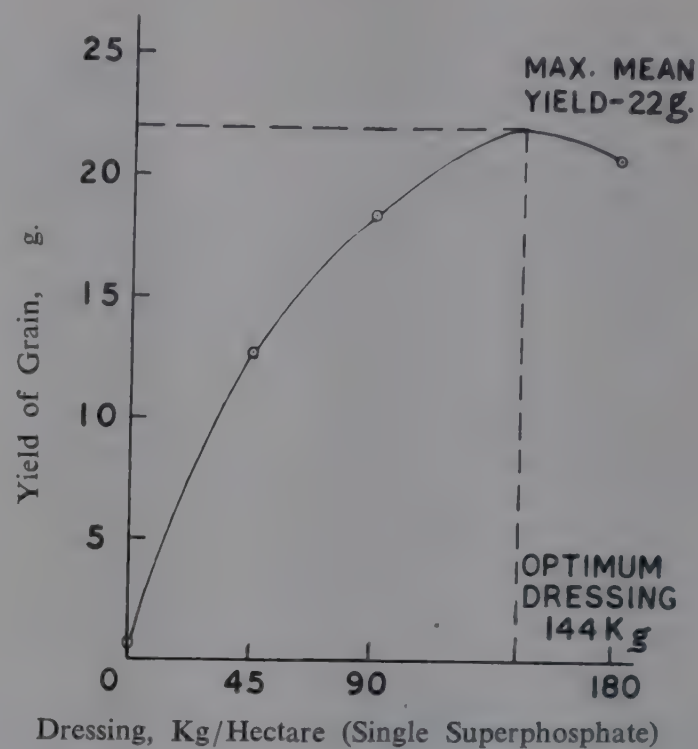


Fig. 3b

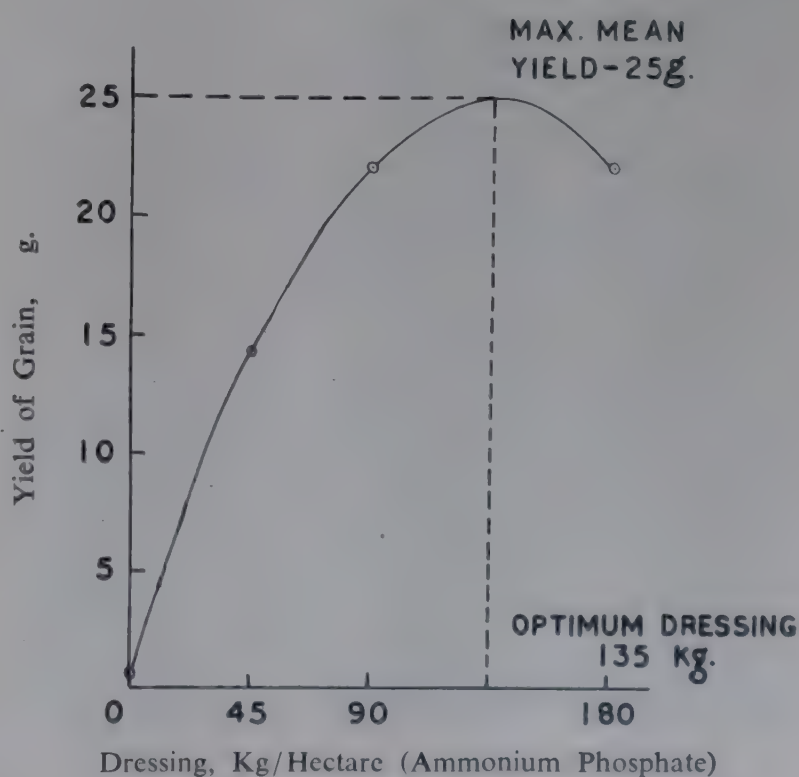


Fig. 3c

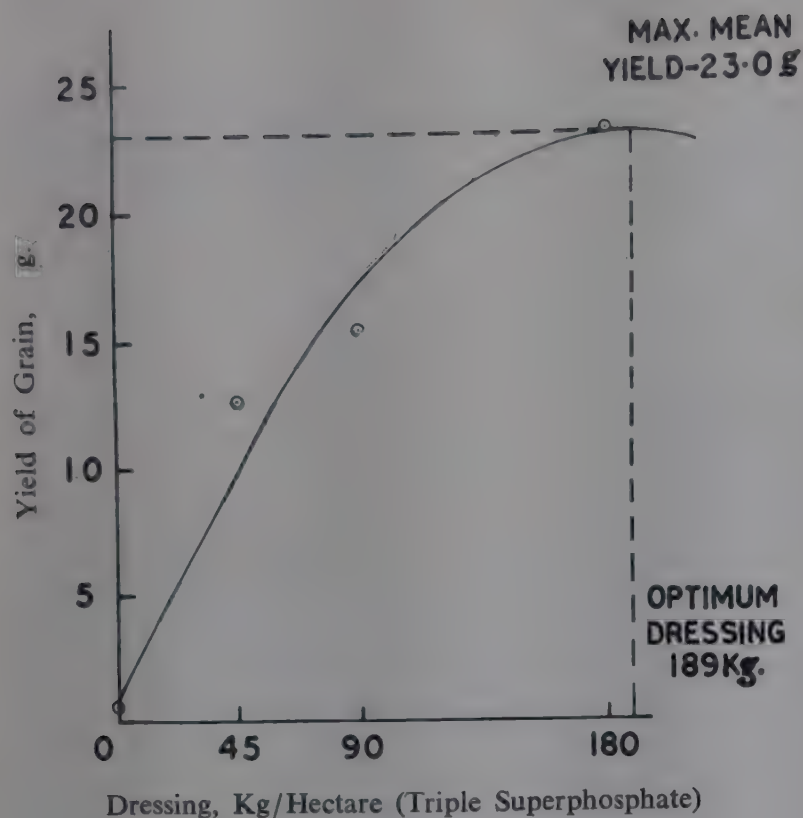


Fig. 3d

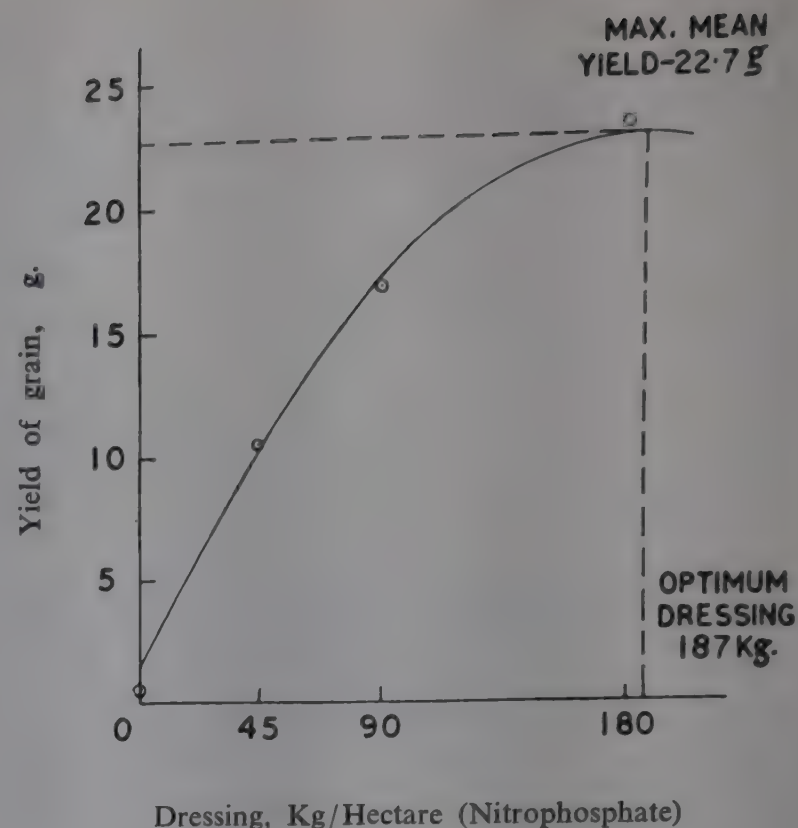


Fig. 3e

Acknowledgements

Thanks are due to Dr. B. K. Dhar and Dr. B. K. Banerjee, Addl. Supdt., for their valuable suggestions throughout the progress of work. Thanks are also due to Dr. S. K. Ghosh and to the Statistics Section of the Central Fuel Research Institute (CSIR), Jealgora (Dhanbad), for the latter's help in statistical analysis of the results.

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[Original mss. received on 12.9.68]

petrographic study of the phosphatic nodules belonging to the Cretaceous rocks of *Tiruchirapalli* district has been made. The study suggests an organic origin of these nodules, suggestive of a calm and quiet water environment.

Phosphatic Nodules of Cretaceous Rocks from *Tiruchirapalli* District (Madras State)

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The phosphatic deposits of *Tiruchirapalli* in a nodular form were discovered about seventy-five years ago. Apart from field and megascopic descriptions along with economic feasibility of these and other associated industrial raw materials, like limestone, gypsum, strontianite, celestite, chalk and clay¹, no detailed petrographic study of these nodules has been reported. These deposits as they appear in the present state do not offer possibilities of industrial exploitation, due to their irregular and sporadic occurrences.

In the light of recent developments in marine geology in the various parts of the world in general, and in the context of India's present need for phosphatic minerals in particular, intensive study of these nodules was undertaken.

Blanford² was the first to undertake a detailed geological mapping of the area and Warth^{3,4} first recognized the nature of the phosphatic nodules and their septarian character. In 1949, Krishnan⁴ made a detailed study of these nodules with respect to their reserves and economic feasibility of mining. According to Rao^{5,6}, about 50 per cent of these nodules consist of calcium phosphate, clay, calcium carbonate, with some ferruginous material and glauconite.

Present Study

These phosphatic nodules occur in the upper part of the *Uttatur* stage, which forms the lowermost stage of the Cretaceous rocks, and are embedded sporadically in gypseous clay which lacks bedding. Due to the soft nature of these rocks, "badland" topography has been developed. The nodules were collected from *Karai* (11.8', 78.53'), *Therani* (11.6', 78.52'), *Nambakurichi* (11.3', 78.52'), *Uttatur* (11.4', 78.1') and *Kunnam* (11.14', 78.1').

According to Pettijohn⁷, "concretions are the product of accumulation of mineral matter in the pores of sediment about a nucleus or centre". In the nodules under study, the nucleus is the cast of the fossil or hollow space left after the solution of the cast. The diameter of the concretions varies from 5 to 15 cm. and most of the nodules are spherical or elongate with a pale brown and pale yellow to a reddish brown colour, depending upon the proportion of iron oxide (Plate I, Photo 1). The interior of these concretions are traversed by radial as well as concentric cracks which have an irregular pattern

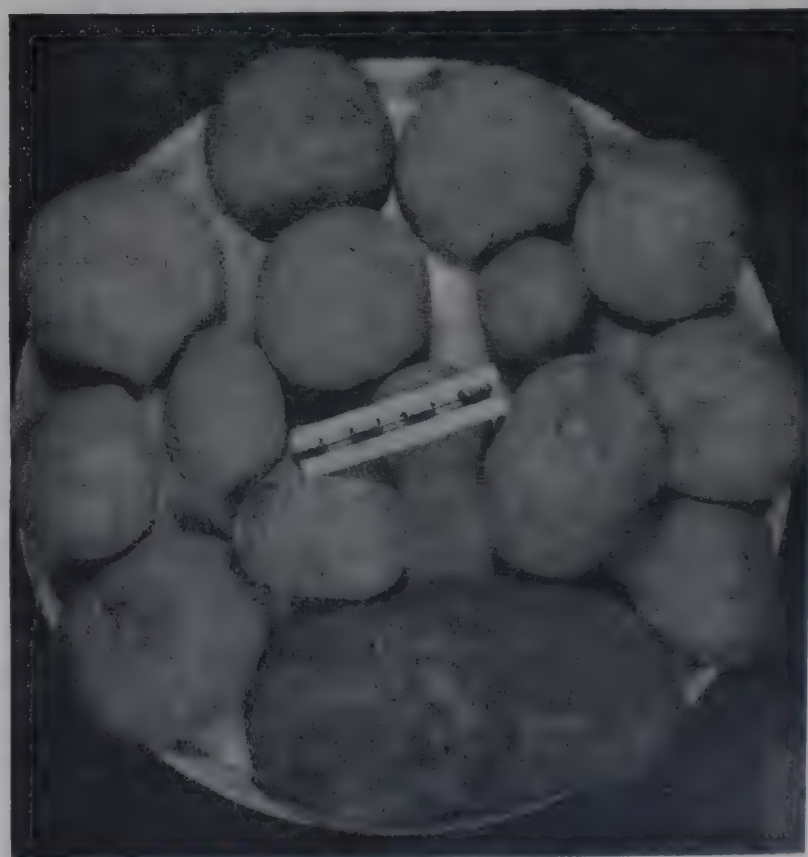


Plate I, Photo I—General Nature of the Nodules.

and are filled by carbonate minerals (Plate I, Photos 2 and 3). In some of the concretions with eroded periphery, the veins stand out prominently and resemble “turtle backs” in which the softer material is leached away. Two types of concretions, namely (i) with a lighter concentric outer laminae around a darker inner core with fecal pellets and fossils (Plate I, Photo 2) and (ii) with concentric outer laminae around the core of dark amber coloured fossil mould (Plate II, Photos 4 and 5) are observed.

A study of the sectioned and polished blocks of the nodules showed that the interior is full of microfossils, glauconite and dark brown pellets, which are floating in a brown matrix. The sizes of the constituents vary from those of clay to granule. Internally the brown colour grades into dark brown colour with a network of mineral veins traversing the brown material in a zig-zag manner. The concretions are very well-rounded, coated with clay materials. The removal of the coating reveals the presence of innumerable pores.

Fourteen thin sections have been studied for the modal composition of the nodules (Table 1).

TABLE 1—COMPOSITION OF NODULES, % BY VOL.

No.	Fossil Fragments	Pellets	Detrital Quartz + Feldspar	Cement (Impure Micrite)	Vein Minerals
1	30.6	7.4	3.4	57.2	1.4
2	24.6	8.8	1.8	42.4	22.4
3	22.5	12.5	1.8	36.7	26.5
4	25.4	7.8	1.4	45.2	20.2
5	22.2	14.0	1.6	41.4	20.8
6	33.4	14.0	0.6	45.4	6.6
7	27.1	13.5	0.5	44.1	14.8
8	26.9	13.5	0.3	44.0	15.3
9	25.75	25.25	0.25	48.5	0.25
10	41.2	10.4	—	46.6	1.8
11	24.6	12.6	0.8	43.6	18.4
12	28.0	19.1	—	37.9	15.0
13	33.5	7.5	1.25	35.5	22.25
14	14.5	4.0	—	25.25	56.25

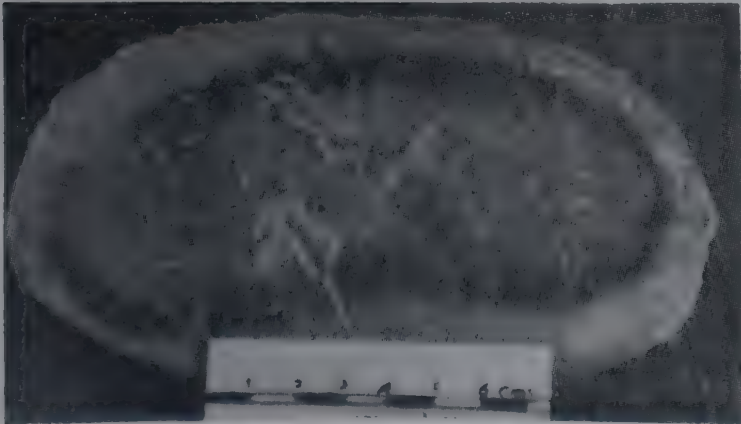


Plate I, Photo 2—Nature of the Vein Fillings.

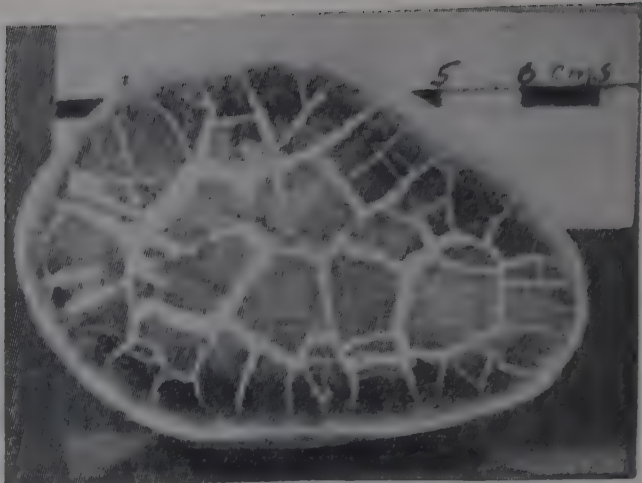


Plate I, Photo 3—Nature of the Vein Fillings.

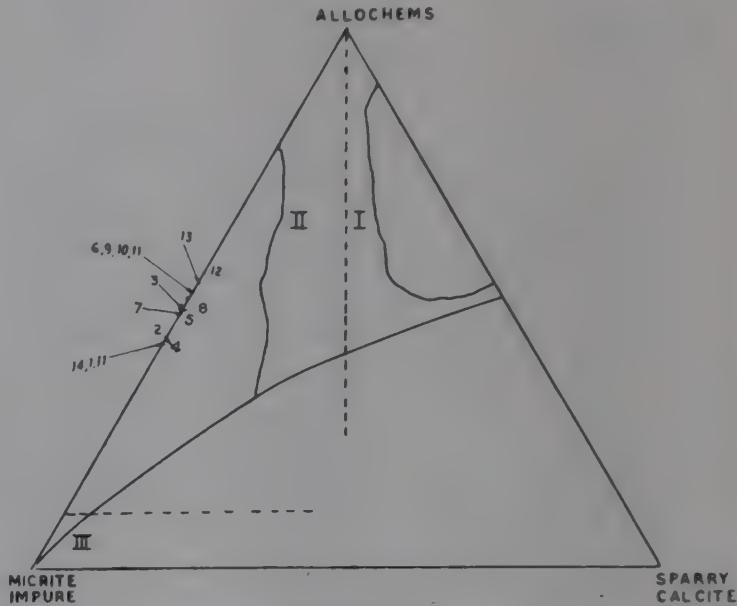


Fig. 1—Classification of Nodules on the Folk (1962) Diagram

The petrographic study reveals that these concretions are more or less uniform in their mineralogical composition as well as textural attribute. The framework is mainly composed of fossil fragments, glauconite and brown pellets, detrital quartz and acid *plagioclase*, which are embedded in a fine-grained brown phosphatized calcareous matrix (Plate II, Photo 6 and Plate III Photo 7). The framework constituents and the impure micritic cement were recalculated to 100 per cent leaving behind the vein minerals. On the basis of the plot in Folk’s triangle⁸ (Fig. 1), the rock falls in Type II limestones (Microcrystalline allochemical limestone).

The ratio (energy index) = $\frac{\text{Allochem} + \text{Mineral Grains}}{\text{Micrite}}$ was calculated and Schenk’s⁹ arbitrary classes are used to decipher the degree of turbulence.

Fossil fragments are dominantly made up of the microfauna-like *foaminifers* as well as the other skeletal parts, which form 14 to 41 per cent by volume of the nodules. The fossil fragments are mostly broken except in a few cases wherein they are entire. In some

ses, they are replaced entirely by recrystallized microcrystalline calcite (Micrite) leaving behind the 'host' of the fossil fragment with brown margin. On the whole, the sorting is moderately good but the fragments are angular. In one or two cases, a beautifully preserved mould of a fossil with a honeycomb structure was observed to form the nucleus (Plate III, Photo 8). In thin section, the brown chambers are elliptical with an outer calcareous rim. The nucleus is also traversed by the latter infilling veins (Plate III, Photo 9).

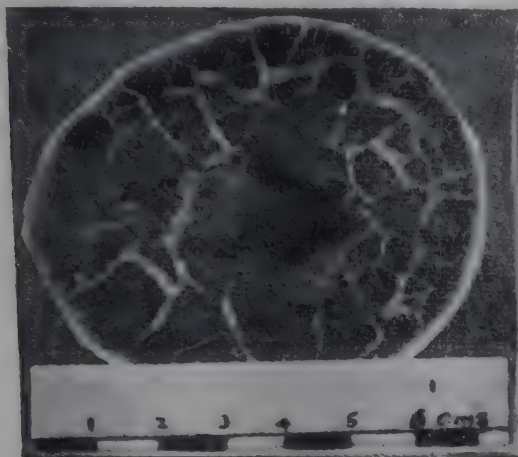


Plate II, Photo 4—Nodule with the Cast of the Fossil as the Nucleus.

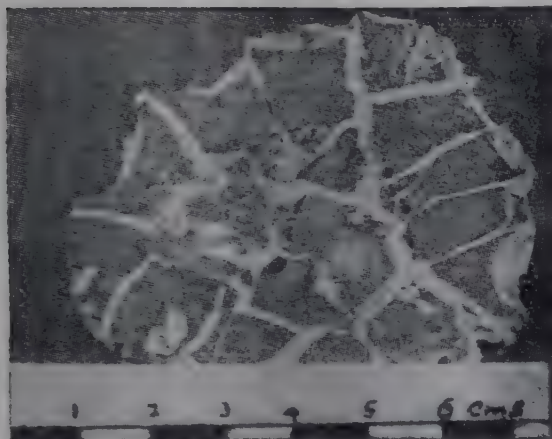


Plate II, Photo 5—Nature of Vein Fillings.

The pellets and glauconite form 4 to 25 per cent by volume of the rock. In some cases, they are seen to cluster the interspaces of the fossil fragments. The terrigenous quartz and feldspar are observed in small amounts and are angular due to corrosion. The vein minerals form 1.4 to 56 per cent of the rock by volume; they are made up of mainly calcite, celestite and gypsum.

The cementing material is microcrystalline calcite, which is fine-grained and partially replaced by a brown phosphatic and ferruginous material in a definite manner. There is no total recrystallization of the micrite material, except in certain cases like fossil fragments. All the framework constituents float in the impure micritic cement,

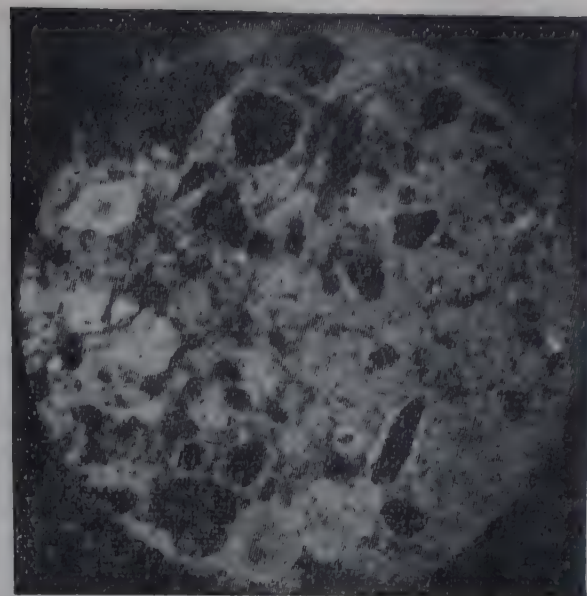


Plate II, Photo 6—General Texture Showing the various Types of Pellets $\times 19$



Plate III, Photo 7—General Texture Showing the Abundant Pellets $\times 5$

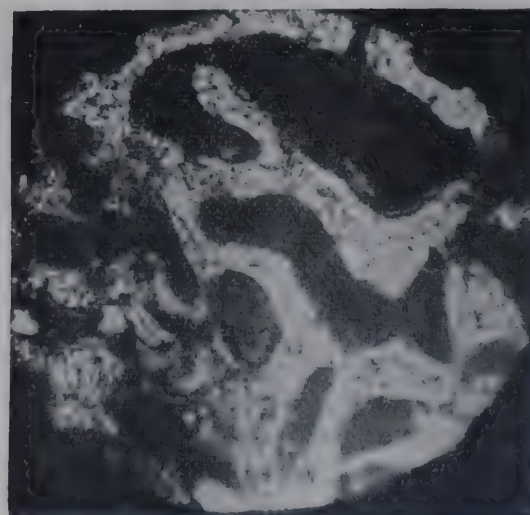


Plate III, Photo 8—Nature of the Chambers of the Fossil Cast Nucleus $\times 19$



Plate III, Photo 9—Nature of the Fossil Cast Nucleus and its Relationship with Vein Minerals
× 5

Discussion

The petrographic study of the polished nodules shows the presence of fossil as nucleus, which indicates that the nodules have been formed due to organic activity of the (skeleton of the) marine organisms. The micritic cement, which is present in a good amount, indicates an environment wherein the wave action is poor. Also, the energy index ratio points to a low turbulence. The nodules are associated with gypseous clay which points to a standing calm and quiet water environment. Some of the fossils which form the nuclei of nodules are similar in all respects to the fossils of the underlying coralline limestone. It is quite probable that the nuclei of the nodules have been derived from the underlying coralline limestone.

A review of the work done regarding the origin of the concretions is presented by Stanley¹⁰ *et al.* Concentrations with fossil nuclei are silty calcareous variety and have been described by Dawson¹¹, Quirke¹², Kindle¹³, Tarr¹⁴ (Stanley¹⁰) and Weeks¹⁵. The nodules under study might have been formed simultaneously resting in the soft clay in which they are embedded and slow growth has taken place or they may be of early diagenetic origin because the framework constituents are floating uniformly in the micritic matrix. The seeding of the concretions took place in the lime-rich zones, nearer them. The carbonate was drawn from the surrounding sediments and well-developed local packets were produced. The precipitation of the carbonate around the fossil nucleus, according to Weeks¹⁵, is due to anaerobic decay of the nitrogenous organic matter which released ammonia and amines that, in turn, elevated the pH, resulting in the concentration of carbonates. Partial phosphatization and accumulation of ferruginous mass

took place at later stages. The phosphatization of these calcareous nodules took place later due to the high calcium concentration and also to the arid nature. According to Strakhov¹⁶ and Bushinski¹⁷, seas of the arid zones are characterized by a relatively high calcium concentration, which stimulates the precipitation of phosphates.

After the formation of the nodules the floor of the basin was uplifted resulting in the decrease of depth, which, in turn, increased the evaporation resulting in the development of evaporite facies, as indicated by the presence of minerals, like gypsum, celestite and strontionite, in a good quantity in these rocks. The arid climate is further indicated by the red clays and red shales as well as red nodules. During the period of evaporation, the nodules' outer surface was hardened with simultaneous dehydration of the interior resulting in the formation of shrinkage crack pattern, which was later filled by the precipitated mineral material.

The underlying coralline conglomeritic limestone, on the other hand, shows an environment in which turbulence and wave action were more, showing the presence of coast line on the western side. Pascoe⁵ also concluded that these beds have been deposited in a moderate depth.

Acknowledgements

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An indirect polarographic method for estimation of biuret (in micro amounts) in commercial urea has been developed.

Polarographic Estimation of Biuret in Commercial Urea

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Estimation of biuret in commercial urea is important because of its poisonous behaviour towards crops and constant association with urea. So far, colorimetric methods^{1,2} were used, but these are often tedious and involve interference due to the many times excess of urea. The present communication, however, records observations on an indirect polarographic method for the estimation of micro amounts of biuret in commercial urea.

In ammonia buffer (pH 9.2), cadmium (II) gives a reversible diffusion wave, the height of which decreases gradually on adding increasing amounts of biuret. The decrease in height was proportional to the concentration of biuret added. Urea, even if it is present in hundred-fold excess, has no effect on the diffusion wave, and hence this method is suitable for estimating microgram amounts of biuret.

Experimental

All the reagents used were of Analar grade. The stock solutions of cadmium (II), ammonia buffer (pH 9.2) and biuret (in KOH) were prepared and used from time to time.

Polarograms were recorded on an automatic recording Cambridge Univector Polarograph unit. The dropping mercury electrode (d.m.e.) was used with mercury pool anode as the reference electrode. Oxygen-free dry nitrogen was bubbled through the solutions to eject dissolved oxygen. All polarograms were recorded at $25^\circ \pm 0.1^\circ\text{C}$. The capillary characteristics were the same as described earlier⁴. The drop-time in the supporting electrolyte at -0.72 V was 5.2 secs. Triple distilled

mercury was filled in the d.m.e. reservoir and the height of the reservoir was kept constant, except during diffusion control measurements.

Results and Discussion

In ammonia buffer ($\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$) (pH 9.2), cadmium (II) gives a well-defined reversible reduction wave (curve I; Fig. 1) having $E_{1/2} = -0.73$ volts. It was observed on adding biuret to this solution that the height of the wave decreases (curve II, Fig. 1). Further, on adding increasing concentrations of biuret the wave

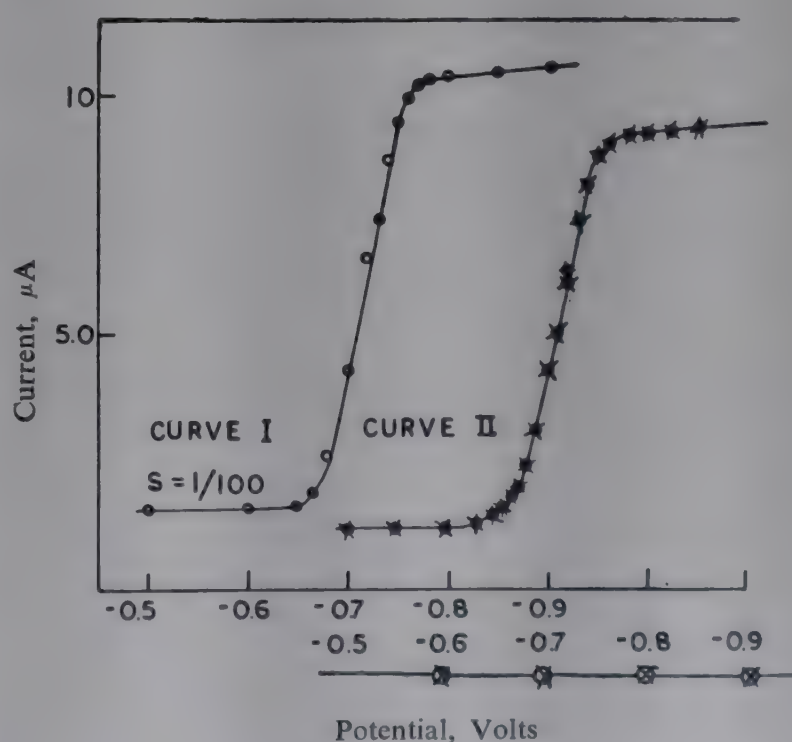


Fig. 1
Curve I—Polarograms of $1.4 \times 10^{-4}\text{ M Cd}^{2+}$
Curve II—Curve I + 2.9×10^{-3} Biuret

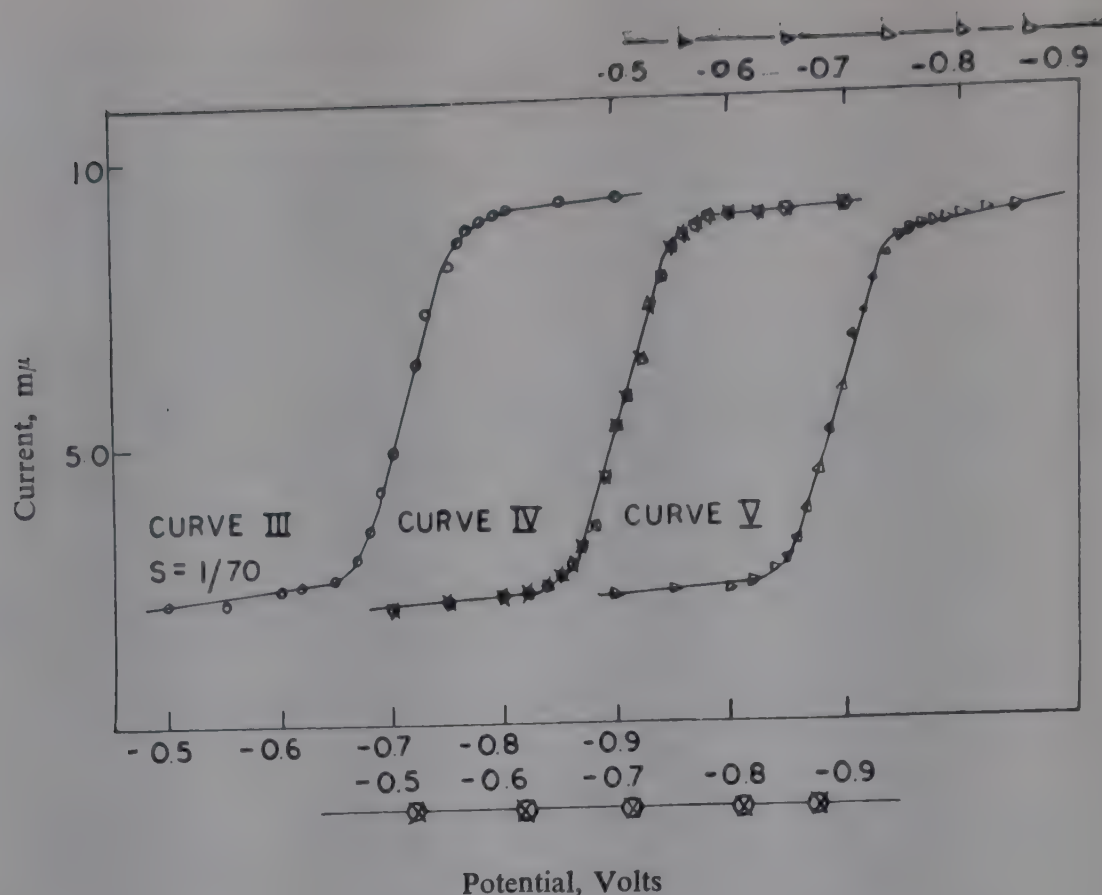


Fig. 2—Polarograms

Curve III—Polarograms of Biuret + Cd^{2+} + 2g. Urea
 Curve IV—Polarograms of Biuret + Cd^{2+} + 4g. Urea
 Curve V—Polarograms of Biuret + Cd^{2+} + 6g. Urea

height goes on decreasing, and the decrease is directly proportional to the concentration of biuret added. However, the $E_{\frac{1}{2}}$ potentials are observed to shift towards more positive potentials on adding the increasing concentrations of biuret, which, according to Vlcek³ et al, is due to dipole formation and to the strong contribution from electrostatic effects towards the rate of the electrode

process. This method has been found suitable for estimating biuret in micro amounts. Further work is in progress.

Effect of Urea: As is evident from curves III, IV and V (Fig.2), addition of even three hundred-fold excess of urea does not interfere with the estimation, i.e. the wave height remains unaltered.

The analytical results are well within ± 2 per cent error and are reproducible. Hence, the method is quite suitable for estimating biuret in commercial urea.

Further studies on the behaviour of electrode reaction are in progress.

TABLE 1—ANALYTICAL RESULTS

Amount of Biuret Taken, g.	Amount of Urea Added, g.	Amount of Biuret Found, g.	Error, %
0.001	2	0.001	0.0
0.01	2	0.0098	-2
0.05	2	0.0495	-1
0.10	2	0.0995	-0.5

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Differential thermal investigation of some 18:8 Cr-Ni steels has been carried out at subzero temperatures (0 to -10°C). In their thermograms at different temperature zones several endothermic bulges have been observed. The appearance of the bulges is attributed to the stepwise austenite-martensite transformations, which are reversible as is evident from both of their cooling and heating curves. Moreover, these bulges as well as the temperatures where they occur in the thermograms are found to be affected by the type of the steel. Molybdenum has an effect on the transformations of 321 and 347 types of steel.

Characterization of Stainless Steels by Differential Thermal Analysis at Subzero Temperatures

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Stainless steels, having about 18 per cent chromium and 8 per cent nickel, are usually austenitic at room temperature. It has been observed by many workers that the austenite of those steels might be partially transformed to martensite by cooling at subzero temperatures or by plastic deformation¹⁻¹⁴. This transformation is usually accompanied by an increase in volume of the steel, although in some cases this change may be very small¹⁵. It has also been pointed out that a ϵ phase is always formed simultaneously with martensite during this transformation. This phase is considered a transition phase in austenite-martensite transformation^{12,13}. The effect of stabilizing and other elements on this transformation has also been studied^{16,17}. Manganese has been found to cause sharp transformation of austenite into martensite at 4-20°K¹⁷. Again, in iron-nickel alloys with low nickel content, the main part in the transformation is played by diffusion processes; on increasing the nickel content, the transformation takes on a more martensitic character. The recrystallization of the austenite is found to be retarded by the introduction of titanium¹⁷. The role of other stabilizing elements in this transformation has not so far been studied in detail.

Sample history also seems to play a part. It has been observed that prestrain in the sample affects the martensite formation on subsequent cooling. But only a small prestrain stimulates the transformation strongly, whereas beyond a certain degree of deformation the tendency for transformation is decreased¹⁸.

The technique of differential thermal analysis has been utilized for studying the order $\rightleftharpoons$ disorder transformation of some alloy systems like gold-copper-nickel alloys¹⁹. But it has not so far been utilized for investigating the transformations of stainless steels. Considering this, an attempt has been made here to study the transformation characteristics of some steels in the subzero temperature ranges by DTA with particular reference to their stabilizing and associated minor elements.

Experimental

Five stainless steel samples of 18:8 chromium-nickel type with different stabilizing elements were taken for this investigation (Table 1). Besides the elements stated (Table 1), these samples are also known to contain

TABLE 1—NON-FERROUS CONSTITUENTS OF STEEL SAMPLES

Steel Sample Sl. No.	Non-ferrous Constituents, %					Type
	Cr	Ni	Mo	Ti	Nb	
1.	20	10	—	0.4	—	321
2.	20	10	—	—	—	304
3.	20	10	—	—	1.0	347
4.	20	10	<0.15	—	1.0	347
5.	20	10	0.15	0.5	—	321

carbon, manganese, phosphorus, silicon and sulphur, but their amounts do not usually exceed 0.08, 2.0, 0.03, 0.75 and 0.03 per cent respectively²⁰.

Linseis ultra-low temperature fully automatic DTA instrument was used for this investigation. Iron-constantan thermocouple was used for measuring the temperature differential as well as the temperature of the sample. The sample-holders were made with a non-ferrous metal—one for an inert material and the other for the sample. Powdered samples were obtained by filling the steels with a previously cleaned V-steel file. The initial filings were rejected. Annealing condition of these steel samples were similar. It may, therefore, be assumed that the prestrains, if there be any, are equal in

all samples. The powder is put in the sample-holder and placed at the top of thermocouple. Inert substance used was α -Al₂O₃. After adjusting the height of the sample-holder the probe containing these was put in a metallic case which was again inserted in a thermostatic bath containing liquid nitrogen. Nitrogen was also passed through the chamber containing the sample and the inert substance. The rates of cooling and heating were controlled by a programme controller. Usually a rate of about 5°C/min. was adjusted in each case. The temperature range used was 0 to -110°C. Both the cooling and heating thermograms of each sample were recorded (Fig. 1); the peak temperatures (Table 2) were correct within $\pm 2.5^\circ\text{C}$.

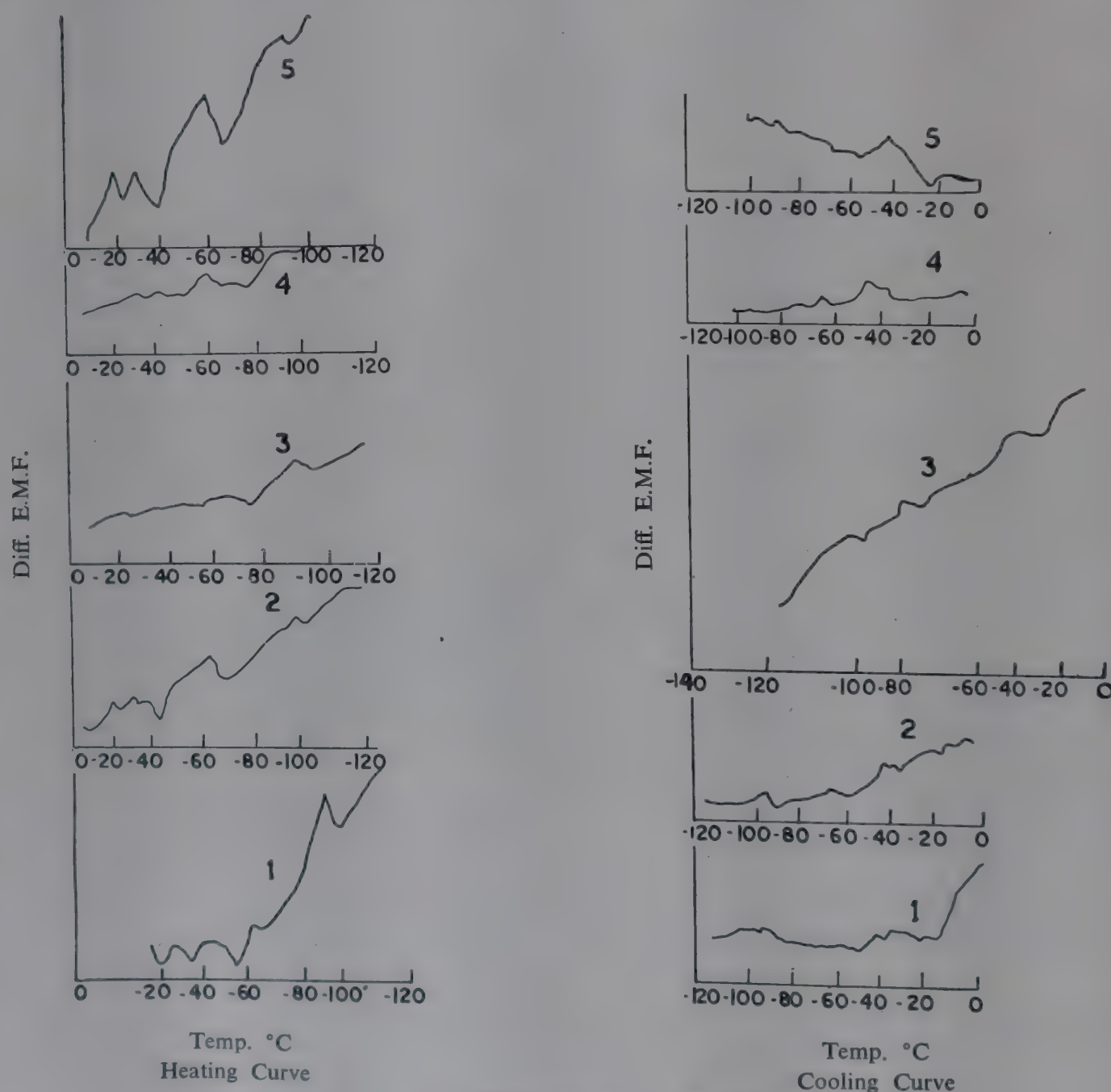


Fig. 1—DTA Thermograms of Steel Samples.

Non-ferrous constituents of samples, %

1—Cr 20, Ni 10 & Ti 0.4; 2—Cr 20 & Ni 10; 3—Cr 20 Ni 10 & Nb 1.0;
4—Cr 20, Ni 10, Mo < 0.15 & Nb 1.0; 5—Cr 20, Ni 10, Mo 0.15 & Ti 0.50

TABLE 2—PEAK TEMPERATURES OF STEEL SAMPLES

Sample No.	Peak Temperature, °C			
	Cooling		Heating	
	Endothermic	Exothermic	Endothermic	Exothermic
1.	-18m, -36m, -54s, -66m, -102s		-18w, -35m, -44m, -60w, -100w	
2.	-10m, -24w, -32w, -44m, -68w, -100m		-10w, -22m, -44m, -68m, -100m	
3.	-24w, -32w, -75m, -98m		-24w, -35w, -75m, -98m	
4.	-34m, -50m, -66m, -76s, -98w		-35w, -50m, -66w, -75w, -98w	
5.	-22m, -40s -66s, -95m		-18m, -40s, -65w, -95w	

s—strong, m—medium, w—weak

Results and Discussion

It is evident from the thermograms of the steel samples that several endothermic bulges appear during cooling at subzero temperatures upto -110°C (Fig.1). On heating the samples subsequently after the cooling stage, the exothermic bulge reappears at the same temperature region as the endothermic bulge (Table 2). This shows that the bulges represent reversible transformations of the samples. As the iron-chromium-nickel steels are austenitic in nature and change to martensite on subsequent cooling at subzero temperatures, these bulges are evidently due to the austenite $\rightleftharpoons$ martensite transformation of the samples. But it is interesting to mention that the peak intensity during heating is less than that during cooling. It indicates that in spite of reversible character of these transformations the observed energy changes in the forward and back transformations are not similar. The reduction of peak intensity during heating may be due to the difference in the thermal conductivity of martensite and austenite phases. Further, the sluggish nature of these bulges may be due to the strain developed in the grains during transformation

which usually causes a change of volume in the specimen because the specific volume of martensite is always greater than that of austenite. Again, the number of these bulges as well as temperatures where they appear in the thermograms are found to vary with the type of steel. Among the three types of steel, viz. 304, 347 and 321, it has been observed that the bulges at -95°C to -102°C are common to all (Tables 1 & 2). Other bulges in the thermograms are in the regions -10 to -44°C and -50 to -75°C (Table 2), which differ not only among the sample types but also in the same type but having different minor elements (Tables 1 & 2). Thus, when 347 type contains molybdenum to the extent of 0.15 per cent, the bulge at -24°C which appears in the same sample without this element is absent whereas additional bulges at -50 and -66°C appear in the former case. Similarly, in case of 321 type steel, the sample containing molybdenum does not reveal any bulges at -18°C and -54°C which appear in the same sample without this element. It may, therefore, be stated that both the steel type and minor elements like molybdenum affect their transformations at subzero temperatures. Further work is in progress to that end.

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X-ray diffraction studies of bulk material and corrosion products from mild steel discharge header of ammonia synthesis gas-compressors showed the formation of oxide and higher hydrated oxide of iron. Erosion of these products results in pitting corrosion.

Corrosion in the Discharge Header of Ammonia Synthesis Gas-Compressors

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A pin-hole leak was observed in the 5th stage discharge header of C. B. Compressor nos. 4, 5 and 9 at the straight portion of a long bend leading to the cross over panel of the ammonia plant, FCI Ltd., Sindri. The visual observation of one sample piece from the damaged region showed the formation of flaky and blackish brown materials on the inside wall of the pipe. Distinct erosion channels were also found in the longitudinal direction of the pipe (Fig. 1). The corrosion was non-uniform and in some places it was found to be even as deep as the entire thickness ($\frac{1}{2}$ ") of the wall itself. X-ray diffraction method of analysis on the bulk material and corrosion products, was taken up to find out the causes of corrosion and leaking.

For x-ray diffraction analysis, the specimen from the bulk material was prepared by drilling and was used as such. In the case of corrosion products, the material was scraped off from inside, powdered and needle shaped specimen of about 0.2 mm. diam. was made with the help of collodion. The x-ray diffraction photographs were obtained in a Debye-Scherrer powder camera of 5.73 cm. diam., using filtered $\text{FeK}\alpha$ radiation. The x-ray diffraction photograph of the bulk material showed

the crystalline phase to be α -Fe, indicating the structure of material of construction to be ferritic and/or pearlitic. The diffraction photograph of the corrosion product was identified to be predominantly α - $\text{FeO}(\text{OH})$ with traces of α - Fe_2O_3 (Fig. 2 and Table 1).

The chemical composition of the m.s. pipe as supplied by the manufacturer was: C 0.21%, P 0.027%, S 0.024%, Si 0.21% and Mn 0.58 per cent. A steeloscopic analysis showed Mn around 0.5 per cent conforming to the above analysis.

The pipe was carrying ammonia synthesis gas at the rate of 8910 cft/min. with the moisture saturated at 1850 psi and a temperature 45°C . The composition of the gas was (in percentage): H_2 —71.5, N_2 —24, CO —3, CO_2 —0.5, CH_4 —0.7 and A—0.3. Normally m.s. pipes are supposed to be corrosion-resistant to the gas mixture of the above type. But if moisture is present along with oxidizing agents like CO and CO_2 , corrosion happens through the following mechanism.

The pre-existing oxide layers on the surface of the inner wall of the m.s. pipe on coming in contact with moisture gives rise to electrochemical corrosion, in which the current is carried by electron mobility through the metal and by ionic mobility through the fluid carried¹. The first corrosion product is FeO , H_2O or $\text{Fe}(\text{OH})_2$. These iron hydroxide layers suffer further oxidation by coming in contact with excess of moisture along with CO and CO_2 present in the synthesis gas and produce a series of higher oxide hydrates of iron^{2,3}, the ultimate



Fig. 1—Inside of the Corroded Pipe



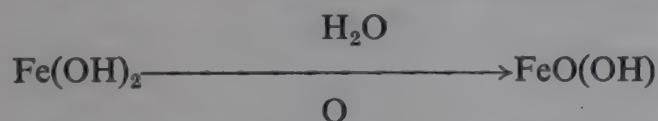
Fig. 2—(a) Bulk Material, (b) Corrosion Product

TABLE 1—X-RAY DIFFRACTION DATA

Bulk Material		α Fe, ASTM, 6-0696		Corrosion Product*		α FeO (OH) ^b		α Fe ₂ O ₃ ^b	
d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁
2.025	s	2.027	100	5.02	w	4.98	15		
1.45	w	1.433	19	4.16	s	4.18	100		
1.182	m	1.170	30	3.67	vvw			3.67	35
1.019	w, br	1.013	9	3.41	vvw	3.38	10		
				3.30	vvw				
				2.80	vvw				
				2.69	m	2.69	30	2.69	100
				2.58	vw	2.58	8		
				2.52	vw	2.52	3	2.51	75
						2.49	15		
				2.46	m	2.45	25		
				2.24	vw	2.25	10		
				2.18	w	2.19	20	2.20	25
				2.09	vvw			2.07	3
				2.02	vvw	2.01	2		
				1.89	w	1.92	6		
				1.84	vvw			1.84	30
				1.79	vw	1.80	7		
						1.77	2		
				1.71	w	1.72	20		
				1.68	vw	1.69	10	1.69	45
						1.66	4	1.64	2
				1.60	vw	1.61	6	1.60	15
				1.56	w	1.56	15		
				1.51	vw	1.51	10		
				1.49	vw	1.47	4	1.48	20
				1.45	vw	1.45	10	1.45	25
				1.40	vvw	1.42	2		
						1.40	7		
				1.36	vvw	1.36	7	1.35	6

*The two lines at 3.30 and 2.80 Å could not be accounted. Probably these may be from α -FeO (OH) itself caused by structural defects.
s—strong, m—medium, w—weak, vw—very weak, vvw—very very weak

product of the reaction being Fe₂O₃, H₂O or FeO(OH).



In fact, the major phase in the corrosion product from the inside wall of the pipe was identified to be goethite, α -FeO(OH) by our x-ray analysis. Formation and accumulation of hydrated oxides which are flaky and porous give rise to pitting corrosion⁴. When this mechanism is continued over a long period, large scale erosion takes place. Gradually, the wall thickness becomes thinner and ultimately the pipe starts leaking.

Therefore, to minimize this sort of electrochemical and pitting corrosion in mild steel pipe lines, carrying specially oxidizing agents, removal of moisture to the maximum is desirable.

Acknowledgement

The authors' thanks are due to Sri R. C. P. Sinha and Sri M. Samaddar for their cooperation in doing the steeloscopic analysis and taking the photograph of the corroded pipe respectively.

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From a study of optical absorption and ESR spectra of zircon, it is inferred that the coloration in zircon arises mainly from the colour centres produced by high-energy irradiation from radioactive impurities present in the crystal.

On the Origin of Coloration in Zircon Crystals

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Zircon crystals are found to vary in colour from deep reddish-brown through light yellowish or greenish-brown to colourless transparency. So far, no systematic study on the origin of the coloration appears to have been made, though it has been suggested that the influence of the sub-facies is the prime factor in determining the colour¹. According to Pigorini² et al, the variation in the colour of zircon crystals can be correlated to the geological age and the thermal history of the sample. But, significantly, they do not mention about the influence of the impurity ions on the coloration, as would have been expected.

The zircon crystals investigated were found to contain Hf^{4+} (ca 1 per cent), Th^{4+} (ca 0.1 per cent) and U^{6+} (ca. 0.01–0.02 per cent) besides which lead and some ions of the iron group of transition metals are present the latter in trace amounts (below 0.001 per cent).

Zr^{4+} , as well as Hf^{4+} and Th^{4+} have got diamagnetic filled shell electronic configurations $4p^6$, $5p^6$, and $6p^6$ respectively, each giving rise to a 1S_0 ground term, which is not split by a ligand field. Their next higher excited states lie too high up to give rise to an absorption band in the visible region.

Uranium sometimes imparts a coloration to its compounds, whose absorption spectra contain a number of distinct bands in the visible region³.

From the crystal structure of zircon⁴, both the zirconium and the silica-sites are those of tetrahedral coordination, the ligands in each case being oxygen ions. If either of these are occupied by ions of the iron group metals in numbers sufficient to impart coloration, their characteristic absorption bands should appear in the optical absorption spectrum. However, their expected concentration will not be high enough to permit observation of their ESR spectra at room temperature because of the poor signal-to-noise ratio.

Besides the above, the coloration can also arise from defect centres, as the findings of Pigorini et al, also seem to indicate. Colour centres produced by irradiation or other means can give rise to sufficiently intense coloration and also ESR spectra often observable at room temperature⁵.

A study of the optical and ESR spectra may, therefore, provide an unambiguous answer to the problem of the coloration of zircon.

Experimental and Results

Three different zircon samples—deep reddish-brown in colour—from one area were studied. All the three gave identical optical absorption and ESR spectra.

The optical absorption spectra (Fig. 1) were taken with a Beckman DU2 spectrophotometer, using thin sections of zircon crystals as samples.

The ESR spectra (Fig. 2) were studied on a Bruker model B-ER 402 X-band spectrometer fitted with a rectangular TE_{102} mode cavity. As the spectrum was anisotropic and the crystallographic axes of the small crystallites could not be easily ascertained, spectra on powdered samples were recorded for the sake of reproducibility and ease of comparison. The ESR spectra were recorded in the first derivative mode. The uppermost trace (a) is for the original sample. The middle trace (b) is for the sample irradiated with x-rays (Cu-K α radiation) for 6 hr. while the lowermost trace (c) is for the sample subjected to a heat treatment for one hour at 1000°C . (Fig. 2). The x-ray powder diffraction pattern of the heat treated sample was compared with that of the original sample to ascertain that no transformation or decomposition had taken place on heat treatment. No such change was detected. The colour, however, was found to a large extent bleached.

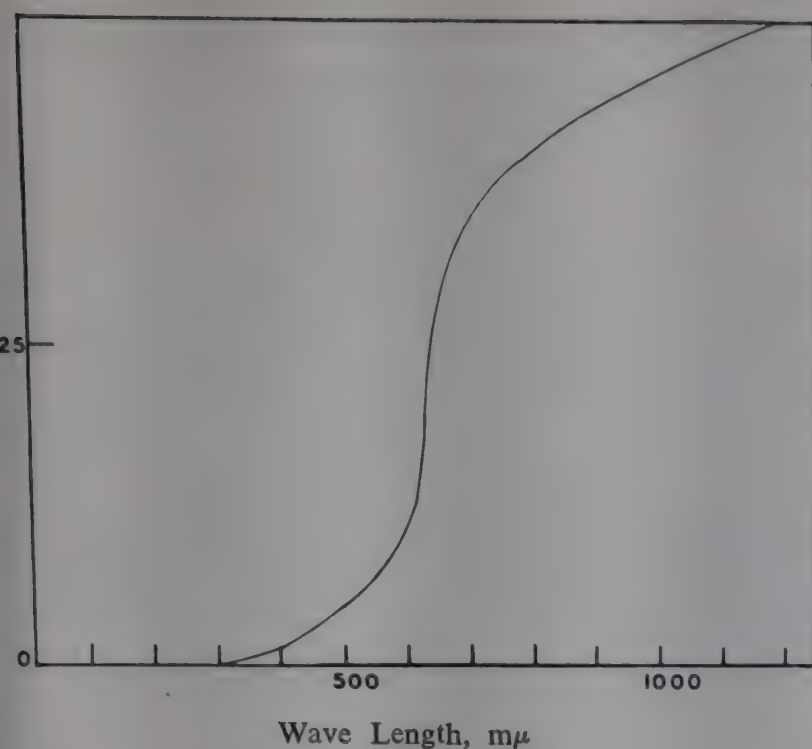


Fig. 1—Optical Absorption Spectra

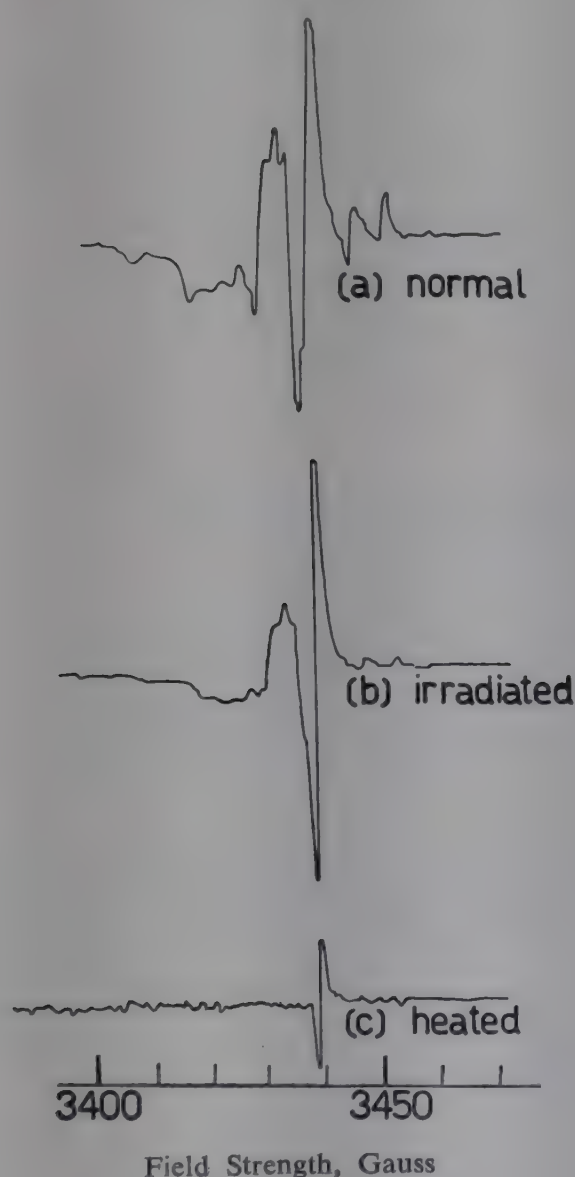


Fig. 2—ESR Spectra.

survived the heat treatment when all the other lines were quenched. The spin density of the original sample was estimated at approximately 10^{20} spins/g.

Discussions

The most conspicuous feature of the optical absorption spectrum is the absence of any peaks. An absorption edge is observed instead, extending from the ultra-violet to $650\text{ m}\mu$, resulting in a reddish-brown coloration of the sample. The nature of this absorption edge is similar to that produced in diamond by irradiation⁶. The absence of absorption peaks indicates that the colour is not due mainly to the impurity of ions directly.

The fact that a strong ESR signal is observed at room temperature is indicative of a large number of paramagnetic centres present in the sample, whose concentration is much higher than that of the impurity ions present. For example, a spin concentration of 10^{19} would mean 1.6 per cent of uranium or 0.4 per cent of copper or 0.1 per cent of chromium, which is absurd.

Also, since Zr^{4+} and Hf^{4+} , as well as Si^{4+} , are diamagnetic, the ESR signals must arise from defect centres, such as produced by irradiation with high energy photons.

A direct evidence in support of this hypothesis is the enhancement of the intensity of one component line of the spectrum by irradiation with x-rays. Possibly, this line arises from an anion vacancy, which traps electrons liberated by the irradiation process, as the line is not quenched completely on heating the sample.

The other lines appear to be due to ions slightly displaced from their original positions. On heating, these interstitial ions diffuse back to their original positions, whereby the lines are quenched. The Lorentzian line shape is in favour of this hypothesis. The spectrum of the powdered sample is complicated by the anisotropy of the lines and further by the presence of Si^{29} (natural abundance 4.7 per cent) and Zr^{91} (natural abundance 11.23 per cent) nuclei, which cause a two-fold and six-fold splitting respectively. Further work on assigning the lines is in progress.

The origin of the colour centres certainly lie in the cumulative effect of the radiation from the small amount of radioactive elements present in the crystal. The observation of Pigorini et al can also be explained on this basis. The concentration of the colour centres is determined by the dynamic equilibrium established between the intensity of the irradiation on the one hand, and the natural tendency of the interstitial ions to diffuse back on the other. As the concentration of the radio-

It may be observed that the intensity of one line was enhanced by the irradiation. It is the same line which had

active elements decreases with age, the equilibrium position shifts, resulting in a change of colour. Thermal history will also obviously influence the colour, as verified by the authors.

Thus, it may be concluded that the colour of zircon crystals largely, if not wholly, arises from the colour centres produced by the effect of radioactive elements present.

Acknowledgements

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Epoxide resins ranging from liquids to solids have been prepared and their properties, such as molecular weight, epoxide equivalent, melting/softening temperature etc., studied. For comparison, the above properties of different epoxide resins marketed under various trade names have been collated.

Epoxide Resins—Their Preparation and Properties

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Introduction

Epoxide resins are mostly condensation products of bisphenol-A and epichlorohydrin. These resins are converted to the thermoset phase when cured with suitable curing agents and have a definite edge over other resins, phenolics, polyesters, acrylics, etc., which are also cured in a similar manner. The comparative usefulness of these resins has itself been revealed by the tremendous developments in them in the advanced countries within a very short time. The works of Castan¹⁻⁴ of Switzerland and Greenlee⁵⁻⁷ of the USA on the preparation of these resins from bisphenol-A and epichlorohydrin in the beginning

of the century are well-known. During the middle of this century, a number of patents⁸⁻¹⁵ both on the preparation of epoxide and its conversion to useful end-products have appeared. Large-scale production started around 1950, which went up to 110 million pounds in 1965 in USA alone.

Epoxide resins are unique materials for coatings, adhesives, spottings, toolings, low pressure mouldings and as stabilizers-plasticizers for vinyl resins. Their wide applications are due to various properties like chemical stability, toughness, quick setting, outstanding adhesion at room temperature etc. attained after curing with

hardeners. Commercially these resins are being marketed under different trade names viz. Epon¹⁶, Epotuf¹⁷, Epi-Rez¹⁸, Araldite¹⁹, etc. in various countries.

Present Work

In view of their varied field of applicability and demand in this country, and also due to non-availability of the processes for their preparation, a study on the preparation of epoxide resins starting from the basic chemicals available indigenously was undertaken. Bisphenol-A was prepared by condensing phenol and acetone at a definite ratio in presence of an acid. After the reaction the unreacted components were distilled off giving a yield of 80-85 per cent bisphenol-A. The latter was purified with organic solvents; its melting point was found to be 155°C.

Epichlorohydrin was prepared from interaction of glycerol and hydrochloric acid gas in a definite ratio at about 110°C in presence of acetic acid. On completion of the reaction, the liquid was neutralized with a base. On distilling this liquid under reduced pressure, α - γ dichlorohydrin, separated as an oily product, which was further treated with dry ether and finely powdered sodium hydroxide at about 15-20°C. The liquid was refluxed under constant stirring at 40-45°C for 4 hours. The mixture was cooled and the ethereal solution decanted. The solvent was distilled off and finally epichlorohydrin was collected within 115-120°C.; its yield was 60-70 per cent.

Studies have shown that the molecular weight of the resins could be increased or decreased by changing the ratio of the bisphenol-A and epichlorohydrin and the resin may be a solid, semi-solid or viscous liquid according to its molecular weight and viscosity. Its preparation involves: (1) reaction of bisphenol-A and epichlorohydrin in presence of an alkali and (2) washing of the resin to make it free from alkali and chloride ions.

The liquid resins were obtained by reacting one mole of bisphenol-A with excess of epichlorohydrin in presence of two moles of sodium hydroxide. The unreacted

TABLE 1—PROPERTIES OF EPOXIDE RESINS PREPARED IN THIS LABORATORY

Sl. No.	State	Melting/Softening Points, °C	Molecular Weight (Osmometer)	Epoxide Equivalent**	Epoxy Group/Ideal Molecule
A*	Liquid	10-20	316	216	1.46
B	Liquid	35-40	507	310	1.60
C	Solid	55-59	825	600	1.37
D	Solid	58-61	930	593	1.56
E	Solid	55-62	900	551	1.83
F	Solid	80-90	1700	875	1.94
G	Solid	78-90	1550	1000	1.50

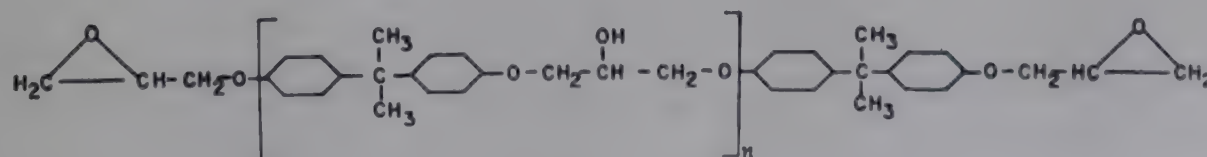
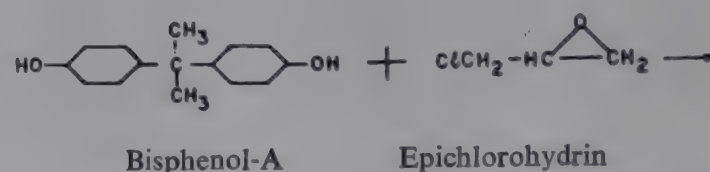
*Distilled product

**By Pyridinium chloride method

components were removed and the resins, made free of chloride and alkali ions, were viscous and amber in colour. The more viscous resins were prepared by increasing the proportion of bisphenol-A but further increase led to the formation of solid resins.

In the preparation of solid resins, after completion of the reaction, the pasty mass was freed of chloride and alkali ions with boiled water under pressure. The solid mass was then freed of water by heating to 150°C and the products, thus obtained, were opaque, brittle and slightly amber in colour.

A generalized structure of the resins is represented below:



Epoxide Resin

Epoxide resin from Epichlorohydrin and Bisphenol-A

The liquid resins having low molecular weights will have an 'n' value ranging from 0 to 1; above 1, the resins are solid.

TABLE 2—COMPARISON OF PROPERTIES OF VARIOUS COMMERCIAL EPOXIDE RESINS WITH THOSE OF THE PRODUCTS DEVELOPED IN THIS LABORATORY

Sl. No.	Manufacturer & Trade Name	Resin No.	Epoxy Equivalent	Molecular Weight	State	Melting/ Softening Points, °C	Viscosity at 25°C, Cp	†Products Prepared in this Laboratory
1. *CIBA CO. 'Araldite'								
		6020	196—208	—	Liquid	—	16000—20000	—
		6030	196—222	—	Liquid	—	25000—32000	A
		6084	825—1025	—	Solid	95—105	—	F and G
		7097	1850—2000	—	Solid	113—123	—	—
2. *Dow Chemical Co.								
		DER 557	1600—2000	—	Solid	113—123	—	—
		DER 661	475—575	—	Solid	70—80	—	C, D and E
		DER 662	575—700	—	Solid	80—90	—	—
		DER 664	875—975	—	Solid	95—105	—	F and G
		QX 2633-18	195—205	—	Liquid	—	18000—35000	—
		QX 2633-19	198—220	—	Liquid	—	23000—41000	A
3. *Jones Dabney 'Epi-Rez'								
		510	180—200	350—400	Liquid	—	10000—16000	A
		515	235—275	460	Semi-solid	20—28	—	B
		520C	450—525	900	Solid	65—75	—	C, D and E
		522C	550—650	1100	Solid	75—85	—	—
		530C	860—1015	1400	Solid	95—105	—	F and G
		540C	1600—2000	2900	Solid	127—133	—	—
4. *Reichhold 'Epo-tuf'								
		37—141	195—205	—	Liquid	—	20000—35000	A
		37—144	230—280	—	Semi solid	20—25	—	B
		37—301	450—525	—	Solid	60—68	—	C, D and E
		37—302	575—725	—	Solid	75—85	—	—
		37—304	875—1000	—	Solid	93—104	—	F and G
		37—307	1550—2000	—	Solid	114—124	—	—
5. *Shell Chemical Co. 'Epon'								
		828	175—210	350—400	Liquid	—	—	A
		834	230—280	450	Viscous Liquid	35—40	—	—
		836	290—335	—	Viscous Liquid	40—45	—	B
		1001	450—550	900—1000	Solid	65—75	—	C, D and E
		1002	600—700	—	Solid	75—85	—	—
		1004	800—1025	1400	Solid	95—105	—	F and G
		1007	2000—2500	2900	Solid	125—135	—	—

*Values have been taken from *Hand Book of Epoxy Resins* by Henry Lee and Kris Neville (McGraw Hill Book Co. Inc., New York), 1967 and *Epoxy Resins* by Henry and Kris Neville (McGraw Hill Book Co. Inc. New York), 1957.

†Values reported in Table 1 of this paper.

An increase in molecular weights and epoxide equivalents changes the physical state of resin from liquid to solid having melting points from 36 to 90°C. (Table 1). Since resins are polymers having different molecular weight species, sharp melting points could not be obtained. The reported data on molecular weights (Table 1) are average values determined by using Mechrolab Vapour Pressure Osmometer Model 301 A. Further, the properties of resins vary widely depending on the methods of their preparation, so that those with similar epoxide equivalent may exhibit different properties, like melting point, reactivity, viscosity, film-forming characteristics, etc. These variations could be broadly assigned to temperature, concentration, ratio and rate of addition of alkali, besides to the ratio of bisphenol to epichlorohydrin. A comparison of the properties of the resins developed in this laboratory with those of the commercial resins of other countries indicates that the former possess almost similar characteristics as the latter (Table 2).

Epoxide resins without hardeners do not possess any industrial applicability. A number of curing agents have already been successfully tried for different industrial uses and reported through patents. However, very encouraging results, so far as chemical stability and toughness are concerned, were obtained in this laboratory with amine hardeners. Further studies on various chemical and physical properties of different modified solutions of liquid and solid resins, particularly for use as acid-resistant coating thereby eliminating the use of imported alloy steels in fertilizer and other industries, are in progress.

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The potency of thionimone—extracted from neem seed kernel—to protect important crops against attack from pests, like red pumpkin beetle, has been studied.

Repellent Properties of Thionimone on Red Pumpkin Beetle *Aulacophora Foveicollis*. L

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Insecticides of plant origin have long been recognised as very effective against insect pests. Since mammals have a high degree of tolerance for these insecticides, these are particularly valued for application on vegetables, fruits and fodders.

Work has been initiated in this laboratory to investigate the potency of neem seed kernel extract, Thionemone, to protect important crops from pest attack. In the present investigation the red pumpkin

beetle—a serious pest for cucurbits—has been taken as a test insect.

Material and Methods

Thionimone was used in the liquid form* as an emulsified concentrate and was diluted with water having six different percentages of the insecticide viz., 10, 5, 3, 2, 1 and 0.5 per cent. These were sprayed uniformly on 35 days old pumpkin plants sown in definite

TABLE 1—MEAN NUMBER OF BEETLES IN EACH PLOT
(Transformed values are given in parenthesis)

Sl. No.	Treatments	After 24 hr.	After 48 hr.	After 72 hr.	After 96 hr.	After 120 hr.	After 144 hr.
1.	10% Thionimone	2.00 (1.56)	4.30 (2.19)	6.60 (2.66)	6.60 (2.66)	10.00 (3.21)	7.60 (2.84)
2.	5% „	7.00 (2.72)	6.00 (2.53)	4.60 (2.26)	7.00 (2.74)	7.30 (2.80)	8.00 (2.91)
3.	3% „	7.60 (2.85)	6.60 (2.64)	7.30 (2.78)	8.00 (2.89)	11.00 (3.38)	6.60 (2.68)
4.	2% „	19.60 (4.49)	8.00 (2.91)	9.60 (3.18)	8.30 (2.96)	23.60 (4.92)	6.30 (2.61)
5.	1% „	7.60 (2.84)	4.60 (2.26)	7.30 (2.78)	7.60 (2.85)	21.00 (4.63)	8.60 (3.02)
6.	0.5% „	13.00 (3.57)	8.30 (2.97)	8.60 (3.00)	17.30 (4.21)	22.30 (4.74)	6.30 (2.61)
7.	Control	77.60 (8.84)	27.00 (5.21)	22.00 (4.74)	16.60 (4.13)	34.00 (5.87)	8.30 (2.96)
‘F’ Value		“Sig” at 1 %	“Sig” at 1 %	“Sig” at 1 %	“Sig” at 1 %	“Sig” at 1 %	“Not Sig”
C.D. at 5 % (of transformed value)		0.89	0.76	0.69	0.50	0.71	—

*Supplied by Messrs Pallishree Ltd., Calcutta

plots. The number of adult pumpkin beetles were collected after 24, 48, 72, 96, 120 and 144 hours separately from each plot and recorded. Each treatment was replicated thrice.

Result and Discussion

A perusal of the data (Table 1) shows that the average number of the beetles in the plots varies significantly in treatments upto 120 hours (5 days) over the control. On the 6th day (after 144 hours), no significant variation was observed among the treatments inclusive of the control. The concentrations 10, 5 and 3 per cent were more effective than the others.

Since the treated plants received practically much

less number of the pests at least for five days, there was an indication that some repellent agent may form a part of the material.

Pradhan¹ *et al* have reported that neem seed kernel possesses extraordinary gustatory-repellent properties for desert and migratory locusts. The same was used effectively to protect wheat seeds against stored grain pests by Jotwani² *et al*.

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2. Jotwani M. G. and Sircar P., (*Indian J. Ent.*, **27** (2) (1965) 160.

This paper analyses the developments the Indian Fertilizer Industry has undergone beginning from the First Five Year Plan to the present state. The future demand, production and likely shortfall of fertilizers with regard to the present conditions have been reviewed. In this connection certain potential sites for the future plants have also been indicated with their product patterns and investments. The authors feel that unless serious attention is given for rapid implementation of the fertilizer projects, it is doubtful that the target demands set for the Fourth plan can be achieved.

Fertilizer Developments in India during Fourth Five-Year Plan Period

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India is passing through an era of agricultural revolution with the growing irrigation facilities, cropping patterns, high-yielding seeds programmes and use of fertilizers. With the increasing demand for food production, the use of fertilizers has become more intense and it is bound to increase during the Fourth Plan period.

The importance of fertilizers in agricultural programmes was felt as early as 1942 following the Bengal famine, when the Grow-More-Food campaign was initiated. Prior to this, fertilizers were mostly used for the plantation crops. An idea of low level of their consumption can be had from the following figures of 1946-47: nitrogen 35,000 te, P_2O_5 4,400 te and K_2O 1,800 te; and by 1950-51 the corresponding figures stood as 55,000, 8,800 and 6,000 tonnes respectively. However, the consumption of fertilizers in India is progressively increasing.

During the First plan, various measures to increase agricultural production were re-emphasized, and the consumption targets of fertilizers by the end of it were set as follows: nitrogen 1,76,000, P_2O_5 68,000 and K_2O 12,000 te. Against this the actual consumptions were nitrogen 1,22,000 and P_2O_5 14,000 tonnes. By the end of Second plan the consumptions achieved were nitrogen 2,10,000, P_2O_5 54,000 and K_2O 26,000 tonnes, against their targets, viz. 370,000, 120,000 and 30,000 tonnes respectively. In the Third plan, the importance of fertilizers in increasing the agricultural production was evident, as was indicated by the consumption targets set for by the end of it, viz. nitrogen 1.0; P_2O_5 0.40 and K_2O 0.2 million tonnes, but these targets were later revised to 8,00,000; 2,50,000 and 1,50,000 tonnes respectively. The consumption of fertilizers during this period was, however, much below. Tables 1 and 2 show the

TABLE 1—CONSUMPTION OF FERTILIZER DURING 1961 TO 1968, M. TONNES

Plant Nutrients	Consumption of Fertilizers						
	1961-62	62-63	63-64	64-65	65-66	66-67	67-68
N	0.250	0.333	0.377	0.492	0.582	0.829	1.047
P_2O_5	0.060	0.083	0.116	0.149	0.134	0.275	0.454
K_2O	0.028	0.036	0.051	0.075	0.090	0.134	0.194
Total	0.338	0.452	0.544	0.716	0.806	1.238	1.695
Per cent increase					12.7	53.6	36.9

(FAI Annual Review 1967-68 (Fert. Assn. of India, New Delhi), 1968 and Estimates Committee¹)

TABLE 2—FERTILIZER CONSUMPTION

	1964-65	65-66	66-67	67-68
Kg./hectare	4.1	4.6	6.9	8.5
Lb/acre	3.7	4.1	6.2	7.6

year-wise consumption from 1961-62 till date and the corresponding figures in kg./hectare.

The targets set for 1970-71 were 2.40, 1.00 and 0.70 million tonnes of nitrogen, P_2O_5 and K_2O respectively. From the rising trend in consumption, the actual consumption figures by 1970-71 may be expected about 1.95, 0.75 and 0.35 million tonnes respectively. The reasons for the shortfall from the targets have been many, but some general types have been pinpointed by the Estimates Committee¹.

The common reasons are untimely receipt of fertilizers, inadequacy of credit facilities for farmers and bottlenecks in distribution arrangements. Taking into account that requirements are being assessed, remedies found and intensive programme planned in the light of newer strategy, it may be inferred that agricultural activities in India are now undergoing a rapid change. Vigorous research activities in evolving high-yielding and highly fertilizer-responsive seeds, soil testing and proper dosing of plant nutrients are afoot to meet the challenge. Package programmes are going to operate mostly in IADP* and IAAP** areas having assured water supply and maximum potential for production in respect of staff and facilities.

Projection of Future Demand

For estimating the targets of consumption during the revised Fourth Plan, the following four methods have been considered: (i) the semi-log method based on fertilizer distribution figures over the past ten years; (ii) the index-rise method based on distribution index for the period 1960-61 to 1967-68; (iii) the population-nutrition method taking into consideration the increasing rate of population and the foodgrains requirements; and (iv) the area-crop method based on the cropping pattern, the distribution of agricultural land under various schemes, irrigation potential and intensive agricultural programme.

The first two methods, based on the consumption trend established through past decade, are graphical representations and therefore the lines are extrapolated

to get the future years' consumption figures. By these two methods, the projected figures give the levels of consumption closer to the line of actuals achieved in the past, while by the third and fourth methods estimates approximate closely the desired levels of consumption.

By the third method, the requirement of foodgrains based on population and the nutritional levels/capita/day is estimated. The fertilizer required for the increased quantum of food production has been calculated on the basis of output-to-nutrient ratio of 10:1, i.e. 10 tonnes of foodgrains per tonne of plant nutrients applied to soil. The year 1964-65 has been selected as the base year and the increased quantum of foodgrain production has been calculated over the production for that year. The nutrient requirement is thus estimated on the above basis and then it is allocated into nitrogen, P_2O_5 , K_2O in the ratio of 4:2:1, which is recommended as the balanced average ratio to be aimed at (Table 3).

The fourth method takes into account the distribution of agriculturable land into irrigated and non-irrigated areas. The non-irrigated area is further sub-divided into (i) areas having rainfall above 45 inches and (ii) those below 45 inches in a year (Table 6). The irrigated area is further divided into areas under high-yielding varieties programme (H.V.P.), non-H.V.P. and non-food crops (Tables 4, 5 & 6). The whole scheme is based on the cropping pattern of a particular year. 1964-65 has been selected the base year as this year records the highest index of agricultural production and productivity amongst the years preceding and following upto 1966-67. H.V.P. has been formulated on the pattern projected for 1970-71. The recommended doses for the cropping patterns are applied to arrive at the total nutrient requirements. Then the results are tabulated year-wise (Tables 7 & 8).

The results of the above four methods have been summarized in Table 9. The average figures are the arithmetical averages for N, P_2O_5 and K_2O , worked out year-wise from 1969-70 to 1973-74. The targeted levels of consumption of plant nutrients have been summarized as average of the four methods during the Fourth plan period (1969-70 to 1973-74) (Table 9). The Food and Agriculture Ministry's† targeted figures for 1973-74 in million tes./year, are as follows: 3.73 nitrogen, 1.73 P_2O_5 , and 1.1 K_2O .

The above figures have been extrapolated upto 1975-76 at the average rate of increase obtained on the basis of consumption figures for the last five years (1969-70 to 1973-74).

*Intensive Agricultural District Programme.

**Intensive Agriculture Area programme.

†Government of India.

Table 4—CROPPING PATTERN OF INDIAN FARMING (1964-65)
(In '000 hectares)

Group	Irrigated	Total
Rice	13,430	36,364
Wheat	4,860	13,460
Jawar	720	17,938
Bajra	295	11,726
Maize	542	4,618
Other cereals and millets	1,706	9,634
Total Cereals	—	93,740
Pulses	2,252	23,793
Total Foodgrains	—	117,533
Groundnut	220	7,216
Sugarcane	1,669	2,562
Cotton	1,259	8,271
Jute	—	839
Total oil seeds	697	15,110
Plantation Crops & Fodder Crop	3,539	1,446
Total cropped area	31,189	159,092

*includes tea, coffee, rubber, tobacco and potato.

[Fertilizer Statistics (Fert. Assn. of India, New Delhi), 1967]

	N	P ₂ O ₅	K ₂ O	Total
1969-70	1.98	0.94	0.47	3.39
1970-71	2.34	1.14	0.58	4.06
1971-72	2.77	1.36	0.71	4.84
1972-73	3.26	1.61	0.87	5.74
1973-74	3.80	1.90	1.08	6.78
1974-75	4.35	2.15	1.28	7.68
1975-76	4.70	2.40	1.56	7.86

Existing Capacity, Production and Additional Capacity by 1973-74

The projected demand by the end of 1973-74 (revised Fourth plan) has been estimated for nitrogen, P₂O₅ and K₂O 3.80, 1.90, 1.08 tonnes respectively. The total plant capacity in production by the end of 1968 stand at 0.904 and 0.434 million tonnes of nitrogen and P₂O₅ respectively. The projects under implementation constitute above 1.784 and 0.892 million tonnes of nitrogen and P₂O₅ respectively (Tables 10 & 11), and they are expected to go into full production by 1973-74; even then

TABLE 3—CONSUMPTION TARGETS OF FERTILIZER NUTRIENTS ON THE BASIS OF PROJECTED POPULATION

Years	Popula- tion, millions	Foodgrains, m. tonnes		Nutrient for Foodgrains, m. tonnes		Total Nutrients, m. tonnes		Total Nutrients Broken Down into N, P ₂ O ₅ & K ₂ O in the ratio of 4:2:1					
								N		P ₂ O ₅		K ₂ O	
								16 oz.	18 oz.	16 oz.	18 oz.	16 oz.	18 oz.
1969-70	549.7	107	120.5	2.36	3.71	3.37	4.72	1.92	2.68	0.96	1.34	0.48	0.67
1970-71	557.0	109	122.5	2.60	3.91	3.70	5.01	2.12	2.84	1.06	1.42	0.53	0.71
Targets worked out in the report of Committee on Fertilizer 1965† for 117 million tonnes of foodgrains for 1970-71								2.41		1.02		0.55	
1971-72	570.0	111	125.0	2.76	4.16	3.93	5.34	2.24	3.06	1.12	1.53	0.56	0.76
1972-73	583.0	114	128.4	3.06	4.50	4.37	5.81	2.50	3.32	1.25	1.66	0.62	0.83
1973-74	596.5	117	132.0	3.40	4.86	4.86	6.32	2.78	3.62	1.36	1.80	0.67	0.90

Basis: (1) The rate of population growth at an average rate of 2.3 per cent/annum.

(2) 1964-65 has been taken as the base year being the good crop year. Foodgrain production in this year was 88.4 million tonnes and application of fertilizer nutrients was 0.716 million tonne including non-foodgrains.

(3) Figures of foodgrains include provision for livestock feed, industry, etc. at 18 per cent of production.

(4) Application for cash crops is assumed to remain same for both the nutritional level.

(5) Output/nutrient ratio as 10:1.

† Report of the Committee on Fertilizers (Ministry of Food & Agriculture, Govt. of India, New Delhi), 1965.

TABLE 5—CROPPING PATTERN AND TARGETED FERTILIZER CONSUMPTION 1973-74 FOR IRRIGATED LAND

A. FOOD CROPS	HVP Area, '000 hectares	Rate of Application, Kg/hectare			Fertilizer Requirement, '000 tonnes		
		N	P ₂ O ₅	K ₂ O	N	P ₂ O ₅	K ₂ O
1. Paddy	8,160	91	57	46	746	465	375
2. Wheat	5,110	91	57	46	467	291	235
3. Jowar	2,600	69	46	34	178	119	88
4. Bajra	2,600	46	34	23	119	88	59
5. Maize	2,600	91	57	46	238	148	119
Total	21,070				1,748	1,111	876
B. FOOD CROPS	Non-HVP Area, '000 hectares						
		N	P ₂ O ₅	K ₂ O	N	P ₂ O ₅	K ₂ O
1. Paddy	10,630	38	25	19	405	266	203
2. Wheat	1,600	38	25	19	63	42	32
3. Other cereals & millets	2,860	38	25	19	109	72	53
Pulses	3,780	11	22	—	41	83	—
Total	18,870				618	463	288
Total food Crops	39,940				2,366	1,574	1,164
C. NON FOOD CROPS							
		N	P ₂ O ₅	K ₂ O	N	P ₂ O ₅	K ₂ O
1. Sugar Cane ¹	2,790	181	78	67	505	233	200
2. Cotton ²	2,110	63	25	11	133	53	23
3. Ground Nut ³	370	17	37	21	6	14	8
4. Total Oil Seeds ⁴	1,170	37	24	12	43	28	14
5. Plantation & Fodder Crops ⁵	5,930	37	24	12	220	140	70
Total	12,370				907	468	315
Grand Total	52,310				3,273	2,042	1,479

1, 2 & 3 are weighted averages for rate of application and 4, 5 recommendations of Sivaraman Committee.

TABLE 6—TARGETED FERTILIZER CONSUMPTION IN RAINFED AREAS IN 1973-74

I. Area having Rainfall over 45"

Crop	Area, '000 hectares	Rate of Application, Kg./ hectare			Fertilizer Requirement, '000 tonnes		
		N	P ₂ O ₅	K ₂ O	N	P ₂ O ₅	K ₂ O
Cereals	2,14,000	25 (Sivaraman Committee*)	12	5	535	250	107
Pulses	5,500	7	14	—	38	76	—
Food Crops	26,900				575	332	107
Non-Food crops	9,600				156	88	28
Total	36,500				724	420	135

TABLE 6—(Contd.)

II. Area with Rainfall below 45"

Crops	Area, '000 hectares		Rate of Application, Kg./ hectare			Fertilizer Requirement, '000 tonnes		
	Rainfall distribution		N	P ₂ O ₅	K ₂ O	N	P ₂ O ₅	K ₂ O
	below 45"	between 35"-45"						
Cereals	48,100	37,200	5	2	—	166	74	—
Pulses	12,400	9,600	3	6	—	28	56	—
Food Crops	60,500	46,800				194	130	—
Non-food crops	21,600	16,800				45	32	—
Total	82,100	63,600				239	162	—
Grand Total	118,600					963	582	135

Summarised Figures for Irrigated and Rainfed Areas

	Area, '000 Hectares			
Irrigated	52,310	3,273	2,042	1,479
Rainfed above 45"	36,500	724	420	135
Rainfed below 45"	82,100	239	182	—
Cultivable land	170,910	4,236	2,624	1,614

*Report of the Committee on Fertilizers (Ministry of Food & Agriculture, Govt. of India, New Delhi), 1965.

TABLE 7—SUMMARY OF CONSUMPTION TARGETS OF FERTILIZER NUTRIENTS BY AREA-CROP METHOD FOR THE TOTAL CULTIVABLE LAND IN 1973-74, M.TONNES

In Irrigated Land:			
Cropwise	N	P ₂ O ₅	K ₂ O
H.V.P. Foodgrains	1.75	1.11	0.88
Non-H.V.P. Foodgrains	0.47	0.31	0.23
Other cereals and pulses	0.15	0.15	0.05
Foodgrains	2.37	1.57	1.16
Non-foodgrains	0.91	0.47	0.31
Total for irrigated land	3.28	2.04	1.47
In Rainfed Land:			
Total for rainfed areas	0.96	0.58	0.13
Grand total	4.24	2.62	1.60

TABLE 8—PHASING OF THE CONSUMPTION TARGETS BY AREA-CROP METHOD, M. TONNES

	N	P ₂ O ₅	K ₂ O	Total
1967-68 (base year)	1.05	0.45	0.19	1.69
1968-69	1.58	0.81	0.42	2.81
1969-70	2.11	1.17	0.65	3.93
1970-71	2.64	1.53	0.88	5.05
1971-72	3.17	1.89	1.11	6.17
1972-73	3.70	2.25	1.34	7.29
1973-74	4.24	2.62	1.60	8.46

TABLE 9—ESTIMATED LEVEL OF FERTILIZER DEMAND FOR THE REVISED FOURTH PLAN (MILLION TONNES/YR.)

Method	1969-70				1970-71				1971-72				1972-73				1973-74			
	N	P ₂ O ₅	K ₂ O	Total	N	P ₂ O ₅	K ₂ O	Total	N	P ₂ O ₅	K ₂ O	Total	N	P ₂ O ₅	K ₂ O	Total	N	P ₂ O ₅	K ₂ O	Total
1st Method																				
Semilong Method based on distribution of past 10 years	1.55	0.52	0.27	2.34	1.95	0.68	0.35	2.98	2.40	0.88	0.47	3.75	3.00	1.15	0.63	4.78	3.70	1.45	0.83	5.98
2nd Method																				
Index of rise method based on distribution. Base year 1960-61 = 100	1.57	0.74	0.28	2.59	1.95	0.93	0.38	3.26	2.44	1.14	0.50	4.08	2.96	1.40	0.67	5.03	3.60	1.75	1.00	6.25
3rd Method																				
Population nutrition basis	2.68	1.34	0.67	4.69	2.84	1.42	0.71	4.97	3.06	1.53	0.76	5.35	3.32	1.66	0.85	5.81	3.62	1.80	0.90	6.32
4th Method																				
Area-Crop	2.11	1.17	0.65	3.93	2.64	1.53	0.88	5.05	3.17	1.89	1.11	6.17	3.70	2.25	1.34	7.36	4.23	2.61	1.57	8.41
Average	1.98	0.94	0.47	3.39	2.34	1.14	0.58	4.06	2.77	1.36	0.71	4.84	3.26	1.61	0.87	5.74	3.80	1.90	1.08	6.78

TABLE 10—FERTILIZER PLANTS LIKELY TO BE COMMISSIONED IN THE IV PLAN PERIOD (1969-70 TO 1973-74) INCLUDING THE PROJECTS APPROVED IN PRINCIPLE

(Grouped according to the likely dates of commissioning)

S. No.	Fertilizer Plants	Month of Commissioning	Capacity in terms of 'N'/yr, '000 tonnes	1969-70	1970-71	1971-72	1972-73	1973-74	1974-75	1975-76	P ₂ O ₅ capacity '000 tes/yr.
1.	Durgapur, FCI	10/69	152	152	—	—	—	—	—	—	—
2.	Cochin, FACT	10/69	152	152	—	—	—	—	—	—	—
3.	Madras Fertilizers*	7/70	170	—	170	—	—	—	—	—	85
4.	Alwaye IV Stage, FACT*	10/69	22	22	—	—	—	—	—	—	9
5.	Baroda, GSFC	7/70	120	—	120	—	—	—	—	—	—
6.	Kanpur, ICI	7/70	200	—	200	—	—	—	—	—	—
7.	Kotah, Sriram*	7/69	130	130	—	—	—	—	—	—	28
8.	Trombay, FCI*	10/71	229	—	—	229	—	—	—	—	124
9.	Namrup Expn., FCI	1/71	152	—	152	—	—	—	—	—	—
10.	Barauni, FCI	1/71	152	—	152	—	—	—	—	—	—
11.	Kandla, Co-operative*	4/72	215	—	—	—	215	—	—	—	127
12.	Morarjee-Kuwait*	8/70	90	—	90	—	—	—	—	—	230
13.	Goa, Birla	9/72	160	—	—	—	160	—	—	—	—
14.	Haldia*	9/73	152	—	—	—	—	152	—	—	136
	Total	—	2096	456	884	229	375	152	—	—	—
	Capacity before 1969-70	—	904	—	—	—	—	—	—	—	—
	Capacity by 1973-74	—	3000	—	—	—	—	—	—	—	—

*Plants having also phosphate capacity of MAP/DAP or Nitrophosphate

TABLE 11—FEATURES FOR PLANTS IN PRODUCTION, UNDER IMPLEMENTATION AND APPROVED IN PRINCIPLE

A—Sectorwise Distribution of Capacity, '000 te/yr.

Sector	In Production		Under Implementation		Approved in Principle		Total	
	N	P ₂ O ₅	N	P ₂ O ₅	N	P ₂ O ₅	N	P ₂ O ₅
Public	689	72	859	133	152	93	1700	298
Private	215	362	710	632	160	—	1085	994
Cooperative	—	—	215	127	—	8	215	135
Total	904	434	1784	892	312	101	3000	1427

B—Capital Outlay, Rs. crores

for the nitrogenous fertilizer plants including N-P₂O₅ complex

Sector	In Production	Under Implementation	Approved in Principle	Total
Public	260	250	53	563
Private	120	170	45	335
Cooperative	—	80	2	82
Total	380	500	100	980

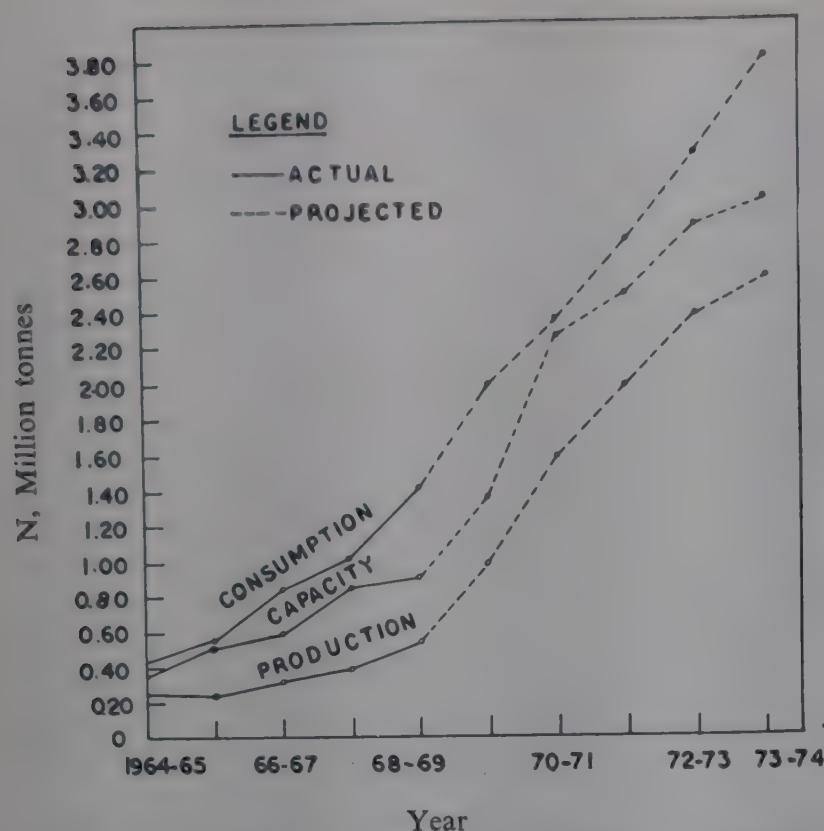


Fig. 1—Consumption Capacity and Production of Nitrogen

there shall be a large deficit by that time. In order to get the production of fertilizers equal to the future demand, installed plant capacity must be in excess to the production capacity and the targeted capacities have been recommended at 4.75 and 2.40 million tonnes of nitrogen and P_2O_5 respectively. The total nitrogen and P_2O_5 capacities expected to be available by the end of 1973-74 revised Fourth plan stand at 3.00 and 1.429 million tonnes respectively. So the additional capacities, which should be envisaged during the Fourth plan, will be 1.75 million tonnes of nitrogen and about 1.00 million tonnes of P_2O_5 .

In view of the above situation some new fertilizer plants have been proposed in this paper. Their location, capacities and feedstock pattern are based on the availability and potentiality of raw materials, utilities, transportation facilities and the market demand. Two broad objectives have been the guidelines in proposing the product pattern for the additional plant capacities for the revised Fourth plan—one the maximum possible exploitation of the indigenous resources and technical know-how and other the high analysis fertilizers consistent with soil condition and optimum economy. In view of the tight position of naphtha as feedstock for fertilizers, the proposed plants have been envisaged to be based on coal, natural gas and heavy distillates of the petroleum industry. Port locations are the potential sites for phosphatic fertilizers plants on imported rock phosphate.

With regard to the type of straight nitrogenous ferti-

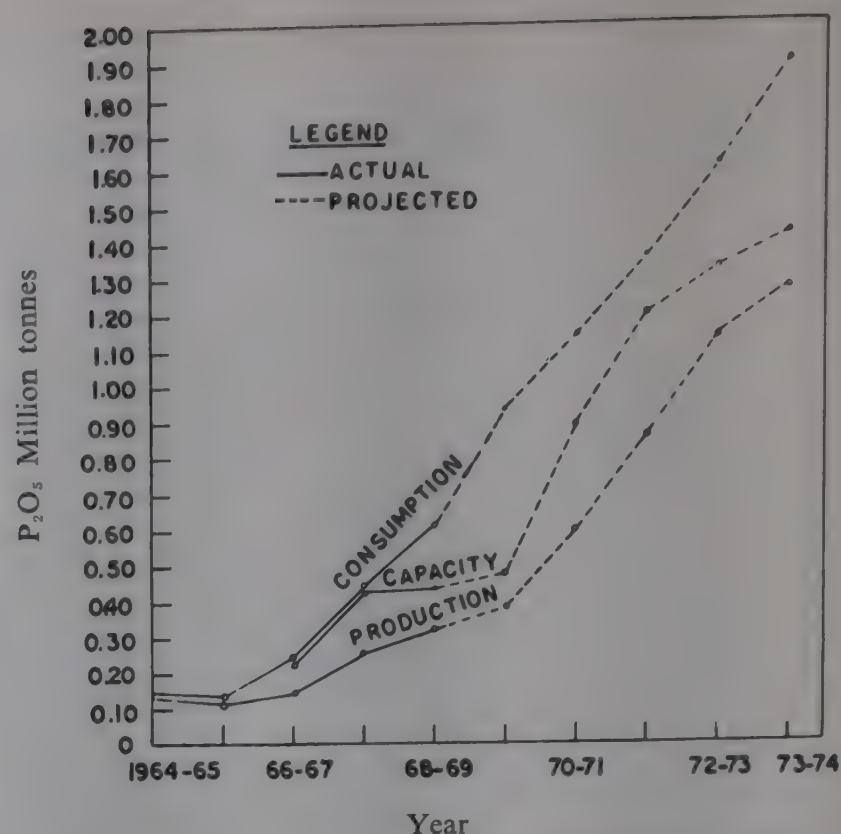


Fig. 2—Consumption Capacity and Production of P_2O_5

lizers, urea has been suggested. The reasons are obvious. Being neutral, it enjoys greater acceptability and can be used in compound fertilizers with a wide range of variations.

In the proposed list of plants (Table 12), four each of 228,000 tonnes nitrogen/year capacity are coal-based, out of which Korba (M.P.), Ramagundam (A.P.) and Talcher (Orissa) are under active consideration of the Govt. of India along with one project at Chanda in Maharashtra. The sites selected for those to utilize the heavy distillates as feedstock are Nangal, Gorakhpur, Mangalore, Tuticorin and Visakhapatnam. The capacity envisaged for each of these is 152,000 tonnes of nitrogen. The other plants, viz. one based on coke oven gas at Ramgarh (Bihar) and the other on new find of natural gas in Gujarat, have also been suggested. The total additional capacity to be covered by the proposed plants during the Fourth plan stands at 1.976 million tonnes/yr. of nitrogen.

For phosphatic fertilizers, process routes are envisaged in conformity with the policy of avoiding the use of sulphur, which has to be imported. The development of the indigenous resources of pyrites may be time-consuming and the beneficiation cost may also be high. The use of sulphur in fertilizer industries is being discouraged because of rising demand of sulphur and the consequent rise in its price in the international market. For the above reasons nitrophosphate has also been suggested as an alternate to TSP which is gaining popularity amongst farmers in many countries. Ammoniated TSP has the

TABLE 12—PLANTS PROPOSED FOR THE FOURTH REVISED PLAN

Raw Material	Plants Location	Capacity, te/N/Yr	Year of Commissioning (Anticipated)	
			1972-73	1973-74
A. Coal	Korba	228,000	228,000	
	Ramagundam	228,000	228,000	
	Talcher	228,000	—	228,000
	Nagpur/Wardha	228,000	—	228,000
B. Natural Gas	Gujarat	152,000	152,000	
C. Coke Oven Gas	Ramgarh	152,000	152,000	—
D. Heavy Distillates	Nangal Expn.	152,000	152,000	—
	Gorakhpur Expn.	152,000	152,000	—
	Mangalore ¹	152,000	—	152,000
	Tuticorin ¹	152,000	—	152,000
	Visakhapatnam ¹	152,000	—	152,000
		1,976,000	1,064,000	912,000
		P ₂ O ₅ te/Yr.		
	Mangalore ¹	150,000	150,000	—
	Tuticorin ¹	150,000	—	150,000
	Visakhapatnam			
	Mashilipatam ¹	150,000	—	150,000
	Talcher/Paradip ¹	150,000	150,000	—
	Saladipura ²	150,000	—	150,000
	Khetri II stage ³	100,000	100,000	—
		850,000	400,000	450,000

1. Port Locations 2. In Rajasthan having pyrite deposits 3. Khetri Copper Project

advantage of being capable of producing a broad spectrum of compound fertilizers in varying analysis of N.P.K. By ammoniation, water-solubility may reduce to a minimum of about 50 per cent. Nitrophosphate has the advantage of process routes not having to use sulphuric acid. Added to this, is the price of nitric acid used in place of sulphuric for N-P fertilizers, which is likely to decline owing to low cost ammonia production. Moreover, with the recent development of sulphate-recycle nitrophosphate route, products of about 80 to 90 per cent water-solubility can be manufactured.

Keeping the above points in view, a few phosphatic fertilizer projects have been suggested in the present study (Table 12). The total capacity of the six plants is 0.85 million tonnes of P₂O₅/yr. If all these projects suggested are commissioned before the completion of the Fourth Plan, their production capacities can be utilized at least by 1973-74.

The phasing of the capital investment for the plants proposed for the revised Fourth plan is given in Tables 13 and 14. The total investment required for the installation of these plants would be about Rs. 730 crores, out of which about Rs. 200 crores in foreign exchange.

The annual requirement of raw materials for rated production capacity of the equivalent ammonia plants proposed for the Fourth plan will be as follows: about 3.5 to 4 million tonnes of coal including that required for process and steam generation; about 0.9 million tonnes of heavy distillates including that required for process and steam generation; about 170 million Nm³ of natural gas and 220 million Nm³ of coke oven gas. The requirement of rock phosphate and elemental sulphur (or its equivalent, viz. 2.5 to 3.2 million tonnes of pyrites) will be of the order of 2.53 and 0.85 million tonnes respectively per year.

Our experience in the past indicates that we were always lagging in fulfilling the targets during the last three plan periods. With the ever-increasing demand for fertilizers in the present plan period, sufficient care should be taken to check the loopholes in our planning of fertilizer industry. Some of the main points of the shortfall in the fertilizer production have been summarized in the Estimates Committee Report¹. However, while planning the projects during Fourth plan, care should be taken to avoid delay in giving clearance to the projects and an all-out effort should be made to imple-

TABLE 13—CAPACITY AND LIKELY PRODUCTION ACHIEVEMENT OF THE PLANTS IN PRODUCTION, IMPLEMENTATION AND APPROVED IN PRINCIPLE FOR THE FOURTH PLAN PERIOD AND CUMMULATIVE EFFECT IN NEXT TWO YEARS

	1969-70	1970-71	1971-72	1972-73	1973-74	Nitrogen in '000 tonnes/yr.	
	1350	2254	2483	2858	3000	1974-75	1975-76
Capacity	976	1570	1977	2361	2568	3000	3000
Production						2658	2681

Increased capacity with additional plants proposed to fill up the gap, assuming the plants to be all commissioned in the latter half of the revised Fourth Plan

	1969-70	1970-71	1971-72	1972-73	1973-74	1974-75	1975-76
Capacity	—	—	—	1064	1976	1976	1976
Production	—	—	—	532	1254	1617	1755
Total capacity	1350	2254	2483	2922	4976	4976	4976
Total production	976	1570	1977	2893	3822	4275	4436

Distribution of the fund required for providing the additional capacity of Nitrogen.

	1969-70	1970-71	1971-72	1972-73	1973-74	Rs. Crores	
						Total	
Capital	60.4	174.2	227.6	106.8	—	569.0	
Foreign Exchange	19.0	54.4	70.8	32.8	—	177.0	

TABLE 14—CAPACITY AND LIKELY PRODUCTION ACHIEVEMENT OF THE PLANTS IN PRODUCTION, IMPLEMENTATION AND APPROVED IN PRINCIPLE FOR THE FOURTH PLAN PERIOD AND THE CUMULATIVE EFFECT IN NEXT TWO YEARS

(i) P_2O_5 , '000 te/yr.

	1969-70	1970-71	1971-72	1972-73	1973-74	1974-75	1975-76
Capacity	478	893	1200	1324	1427	1427	1427
Production	381	599	860	1137	1273	1315	1330

(ii) Increased capacity with additional plants proposed to fill up the gap, assuming the plants to be all commissioned in the latter half of the revised Fourth Plan

	1969-70	1970-71	1971-72	1972-73	1973-74	1974-75	1975-76
Capacity	—	—	—	450	850	850	850
Production	—	—	—	225	537	706	766
Total Capacity	478	893	1200	1774	2277	2277	2277
Total Production	381	599	860	1362	1810	2020	2096

(iii) Distribution of the fund required for providing the additional capacity of P_2O_5

	1969-70	1970-71	1971-72	1972-73	1973-74	Rs. Crores	
						Total	
Capital	18.00	50.00	64.00	28.00	—	160.00	
F.E.	3.40	9.40	12.00	5.20	—	30.00	

ment these within the time-schedule. Top priority should also be given for the import of raw materials, plants and machineries required for these projects. Even if all these steps are taken it is still a big question mark whether we would be able to achieve our targets by 1973-74. The only solution is to go ahead with rapid implementation of more fertilizer plants, so that if not within this plan period at least in the next five year plan we may be self-sufficient in fertilizer production. This, however, may be an extremely difficult proposition, but if India wants self-sufficiency in fertilizer as well as food production, there is no other alternative.

Acknowledgements

The authors' thanks are due to Sarbasri R. R. Poricha and T. R. Ardhanari, Deputy Chief Engineers, P. & D Division, FCI Ltd., for their interest in this work. Thanks are also due to Sri S. N. Roye, Senior Technical Publications Officer, for taking keen interest in going through the Mss. and giving useful suggestions.

REFERENCE

1. *Estimates Committee 1967-68, 49th Report (4rth Lok Sabha)* Ministry of Petroleum & Chemicals, (Government of India)—Fertilizers [Lok Sabha Secretariat, New Delhi], 1968.

In an exploratory experiment two introduced varieties and a local variety of water-melon were tested applying ammonium sulphate plus single superphosphate and nitrophosphate (16:13 grade) with a single level of either 80.0 kg. N or 63.5 kg. P_2O_5 /hectare. The results showed that there was no difference between nitrophosphate and ammonium sulphate-superphosphate combination on equal N and P_2O_5 basis, but both the treatments resulted significantly higher yields over the control. As regards the fruit quality and adaptability of the varieties, Asahi Yamato was found superior to Sugar Baby and the local one.

Effect of Nitrophosphate and Ammonium Sulphate Superphosphate Combination With Three Varieties of Watermelon

Large varieties of water-melon (*Citrulus vulgaris* Schrad) are grown in India for a long time but these are generally of poor quality. Data on the exact manurial requirements of this important crop¹ are not available in India. Hence the two introduced varieties, viz. Asahi Yamato and Sugar Baby, were compared with one local variety in an observational trial to find out the relative merits with the application of nitrophosphate (Carbonitric-16:13) and ammonium sulphate plus superphosphate on equal N and P_2O_5 basis. A single level of 80.0 kg. N/ha. and 63.5 kg. P_2O_5 /ha. was applied. A uniform dose of 50 kg. K_2O from muriate of potash and 10 tonnes of F.Y.M./hectare were also given. The design of the experiment was Randomized Block with four replications having an effective plot size of 5.00 M $\times$ 5.60 M.

Yield

It is evident from the results (Table 1), that Asahi Yamato and the Local were at par but gave significantly higher yields than Sugar Baby.

The interaction between varieties and fertilizer treatments was found non-significant. Both nitrophosphate and ammonium sulphate combined with superphosphate gave higher and significant responses over the control but the former two were found to be at par.

Fruit Size and Edible Portion

From Table 2 it is seen that both Sugar Baby and Asahi Yamato yielded fruits of about 2.8 kg. each, whereas the Local yielded almost double sized fruits.

TABLE 1—YIELDS OF WATERMELONS WITH FERTILIZER TREATMENTS, kg./plot

Variety	Control	Ammonium Sulphate+ Superphosphate	Nitrophosphate	Mean Yield
Sugar Baby	35.7	54.3	59.7	49.9
Asahi Yamato	52.8	89.0	88.5	76.7
Local	53.7	87.7	88.8	76.7
Mean	47.4	77.0	79.0	67.8

C.D. for the treatment means = 14.3 kg./plot

C.D. for the marginal means = 8.3 kg./plot

Both Sugar Baby and the Local produced about 54 per cent edible portion and the same was enhanced by about 4 per cent in the case of Asahi Yamato. As regards the treatment effects, the range of variation of the edible portion is only 1 to 2 per cent.

Skin Thickness, Total Soluble Solids (T.S.S.) and Average Seed Content

The thickness of the skin was lowest in Asahi Yamato but it increased by about 1 and 15 per cent in Sugar Baby and the Local respectively (Fig. 1).

An increase of 28 per cent T.S.S. was found both in Sugar Baby and Asahi Yamato over the local.

The average seed content-fruit was lowest in Sugar Baby i.e. 39.0 g. but it was 55.3g. and 88.6g in Asahi Yamato and the Local respectively.

TABLE 2—AVERAGE FRUIT SIZE AND EDIBLE PORTION OF WATREMELONS

	Sugar Baby		Asahi Yamato		Local		Mean	
	Fruit size, kg.	Edible portion, %	Fruit size, kg.	Edible portion, %	Fruit size, kg.	Edible portion, %	Fruit size, kg.	Edible portion, %
Control	2.4	51.1	3.0	59.0	4.4	56.9	3.3	55.7
Ammonium Sulphate-Superphosphate	2.4	58.4	3.0	57.8	5.0	53.3	3.5	56.5
Nitrophosphate	3.5	52.4	2.7	58.9	4.8	52.5	3.7	54.6
	2.8	54.0	2.9	58.6	4.7	54.2	3.5	55.6

The results obtained indicate that among the three varieties, Asahi Yamato is most suitable for introduction and wide scale cultivation in this tract. It has higher T.S.S. and edible portion, thinner skin and comparatively a lesser seed content as compared to the Local one. Although, as compared to Asahi Yamato, Sugar Baby has also got acceptable fruit qualities, its yield does not encourage much for its recommendation. The economic fruit size coupled with higher yield and better fruit qualities of Asahi Yamato permit the consumers to purchase the whole fruit which is essential from the hygienic point of view also. Regarding the effect of

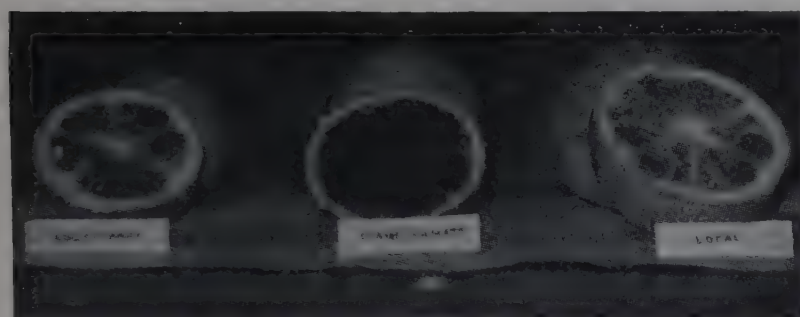
fertilizer treatments, it may be inferred that there was no difference between nitrophosphate and ammonium sulphate+superphosphate combination on equal N and P_2O_5 basis, but both the treatments resulted significantly higher yields over the control. A detailed complex fertilizer experiment is, however, underway with the variety Asahi Yamato, the results of which would be available subsequently.

Acknowledgement

The authors' thanks are due to Sri K. P. Dasgupta, Statistician, for designing the experiment and interpreting the results.

REFERENCE

1. Chowdhury, B., *Vegetables* (National Book Trust, New Delhi), 1967, 129.



Sugar Baby Asahi Yamato Local

Fig. 1—Showing a Comparative Study of Three Varieties of Watermelon.

N. N. BID, P. K. DAS AND S. P. DHUA,
Planning & Development Division,
Fertilizer Corporation of India Ltd., Sindri, Bihar

Technical Digests

Preparation of Sodium Polyphosphate from Trisodium Phosphate^{1,2} or Disodium Hydrogen Phosphate

Sodium polyphosphate finds application in industry as corrosion inhibitor in cooling towers, descaling agent for boilers, deflocculant for various settling slurries and also as water softener and hard surface cleaning agent. Manufacture of polyphosphate is so far based on imported raw materials like sulphur and rock phosphate. Preparation of sodium polyphosphate from indigenous trisodium phosphate available from rare earths extraction plant has been worked out and patented (Ind. Pat. No. 103030). The process is as follows.

Trisodium phosphate or disodium hydrogen phosphate is mixed with ammonium sulphate in suitable proportion and is heated in a pot of sillimanite refractory or in a metallic vessel lined with sillimanite so that a fluid mass is obtained. The hot fluid mass is then quenched by pouring it on another vessel kept cool by water or ice. The product is a solid which contains 28 per cent total P_2O_5 of which 99 per cent is present as sodium polyphosphate.

Another process patented (Ind. Pat. No. 106049) is a modification of the above process and gives a purer product. In this process commercial trisodium phosphate is reacted with 50 per cent (w/w) nitric acid so that the pH of the reacted mass is 7.5 or below and is evaporated to dryness. Sodium nitrate in the dry mass is extracted with the mixture of ethyl or methyl alcohol and water. The solid sodium nitrate (95 per cent) is recovered by distilling off the solvent. The residue obtained after recovering sodium nitrate is mixed with ammonium sulphate and the mixture is heated upto 700°C in a vessel made up of sillimanite to obtain a fluid mass. The hot fluid mass is quenched by pouring on a stainless steel tray kept cool by water and solid sodium

polyphosphate is obtained. The product is a solid mass which contains 59 per cent total P_2O_5 of which 99 per cent is present as sodium polyphosphate.

Effluents from Urea Plants

With rapid growth of industrialization the problem of industrial waste treatment is becoming an overriding task. Foreseeing the need for extensive and all-out effort for disposal of wastes and effluents, the Department of Civil Engineering of the Indian Institute of Technology, Kanpur organized a seminar on Feb. 14-16, 1969, covering the following aspects: characterization of industrial wastes; effects of industrial wastes in environment and beneficial uses of natural sources; industrial waste abatement, reuse and treatment; waste management and system analysis. Sarbasri G. S. Bhattacharyya and G. S. Roy of the water and effluent research section participated in the above seminar on behalf of this Division of FCI Ltd., by reading a paper* and associating in the discussions.

By the end of fourth plan, India would be producing about 3 million metric tons of urea which would account for about 60 per cent of the total nitrogen production, so the problem of disposal of effluents from urea factories would be a tremendous one. The most offensive and difficult to treat effluents of a urea plant are those emanating from urea concentration section containing high amounts of nitrogen both as urea and ammonia. The authors have studied the treatment of these nitrogenous effluents in shallow out-door culture tanks by utilization of a fertilizer species of algae, known as *chlorella pyrenoidesa*, which grow well in a media containing ammonium sulphate, ammonium nitrate, ammonium carbonate or bicarbonate, urea, etc. provided other algal nutrients are supplemented in correct proportions. A typical study has shown that the above algae is not affected appreciably in media containing upto 1100 mg./l. of ammonia nitrogen, tolerance for urea nitrogen being more than 5000 mg./l. (Tables 1 & 2).

1. A process for preparation of sodium polyphosphate from trisodium phosphate or disodium hydrogen phosphate. Ind. Pat. No. 103030 (Inventors: A. K. Roy, R. M. Bhatnagar and K. R. Chakravorty).

2. A process for the simultaneous preparation of sodium polyphosphate and sodium nitrate from trisodium phosphate. Indian Pat. No. 106049 (Inventors: A. K. Roy, R. M. Bhatnagar and K. R. Chakravorty).

*Treatment of Disposal of Effluents of Modern Urea Factories by G. S. Bhattacharyya, G. S. Roy and B. K. Dutta.

TABLE 1—GROWTH AND NUTRIENT UTILIZATION OF ALGAE (PREDOMINANTLY *Chlorella Pyrenoidosa*)
IN DIFFERENT NITROGENOUS MEDIA

Experimental conditions: All the batch experiments were conducted under natural conditions of temperature and daylight using 2 litre culture in 3 litre bottles with 10% CO₂ gas. Only ammonium sulphate medium (A) required alkalinity supplementation which was done by supplying suitable amount of calcium carbonate.

Item	(A) Ammonium Sulphate Medium		(B) Urea Medium		(C) Ammonium Bicarbonate Medium	
	Initial analysis of culture (start), mg./l.	Final analysis of culture after 7 days of algal growth, mg./l.	Initial analysis of culture (start), mg./l.	Final analysis of culture after 7 days of algal growth, mg./l.	Initial analysis of culture (start), mg./l.	Final analysis of culture after 7 days of algal growth, mg./l.
pH	7.0	6.5	7.0	6.4	7.1	6.6
Optical density (as Ex 100)	13	200	13	180	13	165
Total alkalinity as CaCO ₃	660	52	120	176	800	230
NH ₃ -N	200	2	15	4	200	27
Oxidized N	7	2	8	3	8	1
Urea	0.0	0.0	470	62	0.0	0.0
Phosphate as PO ₄ P	34	0.0	34	0.0	34	2.3
Tds on evaporation at 103°C	1300	1260	320	220	350	320
Algae as suspended solid	130	1980	130	1875	130	1620
Total hardness as CaCO ₃	710	700	136	132	136	124
Calcium hardness as CaCO ₃	604	600	63	60	65	63

TABLE 2—GROWTH OF ALGAE (PREDOMINANTLY *Chlorella Pyrenoidosa*) IN MEDIA CONTAINING INCREASING CONCENTRATIONS OF UREA

Experimental conditions: All the batch experiments were conducted at outdoor temperature and at natural daylight of the winter months with 1 litre of culture in 2 litre conical flasks kept on a platform outside the laboratory windows using 10 per cent CO₂ gas. On occasions at midday temperature control was necessary.

Culture No.	Concentration of Urea in Media, mg./l.	Algae Concentration, 100 × optical density (Ex 100)*				
		Start	1 day	2 days	3 days	4 days
1	500	43	69	99	132	155
2	1000	44	70	102	134	160
3	1500	42	66	95	126	156
4	2000	43	67	90	124	154
5	3000	43	68	93	127	157
6	4000	42	65	95	122	151
7	5000	41	63	93	125	153
8	6000	41	59	82	114	141
9	7000	42	66	88	122	156
10	8000	43	75	104	140	164
11	9000	44	68	95	128	157
12	10000	44	68	95	128	157

*Optical density was measured as Ex 100 in photoelectric colorimeter using 1 cm. light path and wave length of 600 mμ.

The principal steps involved in this type of treatment are as follows: segregation of nitrogenous effluents from other effluents and collection in a hold-up tank where their fluctuating qualities are evened out. The effluents are then pumped into shallow algae culture tanks of suitable dimensions where carbon dioxide-enriched air is bubbled at a rate to maintain the algal cells in suspension and that of pH of the culture at 6.0—6.5. Other algal nutrients are fed in correct dose directly into the tanks, which can be operated continuously or batch-wise. An average algal growth rate of 150-200 mg./l./day corresponding to 15—20 mg./l./day of nitrogen removal

are expected from these out-door tanks depending upon the seasons. Of all the nutrients demand for carbon is maximum for the algae, so adequate supply of carbon in the form carbon dioxide-enriched air is essential. 1g of nitrogen removal would require about 200—250 l. of 10 per cent carbon dioxide, which includes a loss of 50—60 per cent of the gas supplied which, however, can be minimized by improved carbon dioxide diffusion devices. After separation of the algae, the effluent from such tanks may either be recycled to the tank or discharged into the sewers, if nitrogen level is sufficiently low.

Notes & News

Carbamate Recycle Process Cuts Urea Costs

In order to meet the increasing world demand for urea, the industry has moved towards much larger capacity than in the past. There are now a number of urea plants under construction which are 300,000 ton/yr and larger; such plants require no more instrumentation, personnel or laboratory facilities than a small one. A major step towards lowering plant cost and utility consumption occurred when a radical change was made in the method of returning the ammonia and carbon dioxide (as a liquid carbamate solution) that was not converted to urea back to the reactor total recycle. Formerly these decomposition products were separated using monoethanolamine or other solvents and returned separately to the urea reactor. Chemico is currently designing and constructing several large single train urea plants using the liquid carbamate recycle process and before offering such plant it had to overcome problems of design of some of the equipment items.

The gas volumes in plants of 300,000 ton/yr capacity are large enough for several stages of centrifugal compression to be used efficiently. Centrifugal compression of upto 3 stages can be used without the discharge flow rate falling below the minimum. The number of stages actually used will vary with such factors as steam balance and the most economic selection of the combination of centrifugal and reciprocating machines.

Considerable experience is required in order to learn the correct combination of operating variables and vessel design that will give a minimum reactor size for any designed degree of conversion of ammonia and carbon dioxide to urea.

In the liquid recycle plants, the unconverted carbon dioxide combined with ammonia and water forms a carbamate solution which is returned to the reactor. For this special high pressure reciprocating pumps are required and because the fluid is corrosive the proper sizing selection of the equipment is vital. It is possible to obtain single units large enough to provide the carbamate pumping requirements for a

330,000 ton/yr. urea plant, but for large plants multiple pumps are required.

To concentrate the 70-75 per cent urea solution produced in the synthesis section to 95 per cent either evaporation or crystallization may be used and because of size and process considerations more than one evaporator are required in large plants but a single crystallizer can be used for 330,000 t/yr a larger plants. For prilling, cylindrical concrete towers have proved less expensive for large towers than rectangular aluminium construction; erection time is also shorter. The air intakes and outlets must be carefully located and sized to produce the uniform air-distribution required to maximize air-prill contact for good heat exchange.

Consideration must also be given to the layout of piping in these sections subject to biuret formation, because long residence time enhances such a formation. Piping runs must be kept at minimum lengths.

The Fundamental Principles of the Ratio between Nitrogen, Phosphate and Potash in Compound Fertilizers

The question of the optimum $N:P_2O_5:K_2O$ ratio of a fertilizer for plant cultivation continually fluctuates. The nutrients in the plants ready for harvesting can be assumed to follow approximately the following ratio:

$$N:P_2O_5:K_2O = 1:0.3-0.4:1.2-1.6$$

Certain limits can of course be established within these limits according to the yield and the type of plant. For example cereals and grass take up a lot of phosphate, potatoes a lot of potash and leguminous crops more nitrogen. Results of experiments carried out over a number of years in moderate climate show that the amounts nutrients obtained from the soil are about 7-10 kg/ha of P_2O_5 and 25-40 kg/ha of K_2O . These amounts can be fully taken into account in the nutrient balance as well. Free-living soil bacteria fix an average of about 15 kg/ha of nitrogen/year. The amount of nitrogen recovered from precipitation can be assumed to be 8-10 kg/ha a year.

Experiments carried out over 50 years have shown that only up to about 50% of the phosphate fertilizer applied is utilized by the plants even over extended periods. The utilization even drops to about 15% or lower on soils which are very deficient in nutrients, very acid or contain too much lime.

Potash, too, reacts with soil colloids. It is well known, for example, that clay minerals are transformed by potash being discharged from groups of layers in the crystals lattice. These clay minerals which are low in potash have the property when swollen of taking up potash again and fixing it so that it is not available to the plants. Furthermore, in very light soils potash is subject to leaching. For these reasons only 80% of the potash can be reckoned in the balance.

Calculations show that a compound fertilizer which is to meet the varied environmental factors in agriculture must roughly have the $N:P_2O_5:K_2O$ ratio of 1:0.6-1.5:1.0-2.0. This ratio is confirmed by the results of numerous fertilizer experiments.

Compound fertilizers are usually broadcast in spring at the beginning of the vegetation period. Where there is a high consumption of nitrogen it is normal to make a second or even third application in the form of straight nitrogen fertilizers a few weeks later. This can further narrow the $N:P_2O_5:K_2O$ ratio of the overall fertilization of a field. These ratios where nitrogen is the predominant nutrient are used particularly in countries where there is a lot of pasturage (England and Holland) and where phosphate and potash are traditionally used sparingly (U.S.A.) by employing special methods (e.g. band fertilization).

Statistics for fertilizer sales show similar figures. For example the average fertilizer $N:P_2O_5:K_2O$ ratio is as follows: in West Germany 1:0.9:1.2 (1966-67); France 1:1.4:1.1 (1965-66); the Netherlands 1:0.4:0.4 (1965-66); Belgium 1:0.9:1.2 (1965-66); England 1:0.6:0.6 (1965-66); the U.S.A. 1:0.7:0.6 (1965-66); and Japan 1:0.7:0.8 (1965-66).

If the conditions existing in Central Europe are taken the following three nutrient ratios are generally sufficient 1:1.5:2, 1:1:1.6 and 1:1:1. Under other climatic conditions and with other crops and crop rotations and taking other factors on the farm into consideration other formulations may be necessary, for example, 1:0.5:0.5, 1:1:0, 1:0.5:1 or even 1:2:3 or 1:3:3. When the soil has a certain nutrient reserve, one can always manage with a few standard formulations.

Any anxiety that this simplified method of fertilization will affect yield and quality is unjustified. On the contrary, it may even promote people's understanding of fertilization, prevent mixtapes being made and thus contribute to lowering costs.

[*The World of NPKS*, No. 28, (1968), 16]

Low-Pressure Methanol Plant

A new catalyst formulation developed by ICI enables it to offer a low pressure methanol plant which substantially cuts both capital and operating costs. The Billingham plant of 100,000 tons/year capacity run by ICI for more than 21 months has operated without recharging the catalyst and it is the first methanol plant to use a centrifugal compressor. Methanol is manufactured by naphtha or natural gas and carbon dioxide.

The feed stock is preheated, desulphurised, mixed with steam and passed to a reformer at a temperature of approximately 400°C. The reformer may be fired by any conventional liquid or gaseous fuel, being supplemented with purge gases and by-products from the process. Waste heat is recovered from the reformer flue gases by steam raising and superheating. The reformed gas is cooled, the waste heat being used for steam raising and feed water heating, and the process steam condensate is removed. The cooled gas is compressed in a centrifugal machine, mixed with recycle gas, preheated and passed to the methanol converter. The converter effluent gas is cooled, condensed methanol is removed and the remaining gas is recycled to the converter by a centrifugal circulator. The condensed crude methanol is led down through a flash drum where dissolved gases are removed, and passed to atmospheric storage. It is then pumped through two distillation columns operating at approximately atmospheric pressure. Light ends, containing dimethyl ether, esters, ketones and iron carbonyl, are removed as a vapour from the first column and water

ESTIMATED MANUFACTURING COST IN £/TON OF 165,000 t/a METHANOL PLANT USING THE LOW PRESSURE PROCESS AND NAPHTHA FEED STOCK (Capital Cost £ 2.85 m.)

	Unit price	Quantity/ton Methanol	Unit Cost £/ton Methanol
<i>Raw Materials</i>			
Naphtha Feed	£8/ton	0.52 ton	4.16
<i>Utilities</i>			
Fuel	£ 0.75/10 ⁶ Kcal	2.9 × 10 ⁶ Kcl	2.18
Electricity	1.2 d./kwh	40 kwh	0.20
Boiled feedwater	18 d./ton	1.9 ton	0.14
Cooling water (10°C rise)	0.5 d./ton	260 ton	0.54
Catalysts			0.54
			7.76
<i>Direct Costs</i>			
Labour and supervision			0.11
Maintenance			0.69
Overhead			0.80
<i>Fixed Costs</i>			
Depreciation and interest			2.59
Total Manufacturing Cost £/Ton			11.95

Notes—Labour and supervision assumes 3 men-shift at £ 1,250/year per man with 20% supervision. The maintenance cost is taken as 4% of the capital cost. The overhead cost is taken as 100% of the combined labour and maintenance costs. Depreciation is taken as 10% of the capital cost with an average interest rate of 5%.

ESTIMATED MANUFACTURING COST IN £/TON OF 165,000 t/a METHANOL PLANT USING THE LOW PRESSURE PROCESS AND NATURAL GAS FEED STOCK (Carbon dioxides used 174 Nm³/ton methanol £ 2.60 m.)

	Unit price	Quantity/ton Methanol	Unit Cost £/ton Methanol
<i>Raw Materials</i>			
Natural Gas	£ 6/1000, Nm ³	640 Nm ³	3.85
<i>Utilities</i>			
Fuel	£ 0.5/10 ⁶ Kcal	3.2 × 10 ⁶ Kal	1.60
Electricity	1.2 d./kwh	44 kwh	0.22
Boiled feedwater	18 d./ton	1.25 ton	0.09
Cooling water	0.5 d./ton	280 ton	0.58
Catalysts			0.50
			6.84
<i>Direct Costs</i>			
Labour and supervision			0.11
Maintenance			0.63
Overhead			0.74
<i>Fixed Costs</i>			
Depreciation and Interest			2.37
Total Manufacturing cost £/Ton			10.69

and higher alcohols (fusel oil) are removed from the bottom section of the second column; purified methanol is removed as a vapour from the top trays of the second column.

The relatively low conversion temperature and pressure permit the use of a hot-wall converter, allowing the saving of the cost of a separate inner vessel and eliminating the need for a full bore closure. On the pressure vessel to allow the removal of the inner vessel. The converter is a quench type, but the quench gas is injected directly into the mass of catalyst using a special patented distributor. When the converter is charged with the catalyst the catalyst particles passed freely between the hollow bars of the distributor until the space is filled. When the converter is in use, perforation in the hollow bar presents to the moving reaction mixture a path which is less obstructed between the catalyst particles, hence the mixture passes preferentially into the interiors of the bars and there mixes with the quench gas to achieve the required temperature. Distribution of gas by these "lozenges" is highly effective, yet they occupy less room than conventional distributors and impose less pressure drop on the gas stream. The catalyst is discharged by operating a door at the bottom of the converter and letting the whole charge run out. Entry into the vessel is not necessary until after discharging, which is an advantage when the catalyst is pyrophoric. No dismantling of internal fitting is necessary.

[*Brit. Chem. Engng.*, 13 (11) (1968), 1512]

Optimum Projection of Exchangers in Ammonia Synthesis

Heat exchanger optimisation, converter, removal and utilization of reaction heat in synthesis loop are some of the subjects which contribute to the economics of the ammonia manufacture. Sebor and colleagues have analysed this problem. They take into account of the type of synthesis loop, the influence of the operating pressure, cost of compression of synthesis gas, the low temperature cooling of the gas mixture, the type of cooler, the influence of the temperature differences upon the heat transfer equipment, the relation between heat transfer and pressure drop and other factors affecting the optimisation problem.

The types of cycle considered in this treatment include those with (a)•fresh gas

feed before the low temperature exchanger; (b) fresh gas introduced before the reactor; (c) no utilization of waste heat; (d) with waste heat boiler; (e) steam produced in the reactor. Whatever circuit is employed affects the choice of exchanger; e.g. it is closely connected with the solution of the steam generated problem; until recently the practice was to use a water cooled exchanger regardless of the production or non-production of steam in the cycle. But the storage of water for cooling purposes poses the problem of the choice of the cooling medium, air or water. For a converter which operates without generating additional steam, the synthesis gas mixture will enter the cooler with a relative high temperature and an air-cooled exchanger may well be a better choice despite the higher investment demanded. Here, the possibility of additional water cooling also enters the picture, since variations with climatic conditions with air cooling alone could reduce the output from the synthesis cycle. If, however, the converter makes additional steam the decision becomes more difficult; a balance has to be struck between the operational reliability of the exchanger and its cost. In the third situation, where steam is produced within the converter as a result of temperature control of the reaction, economic factor solely may decide the type of cooling to be used.

One of the conclusions arising from this contribution is that reducing the ammonia concentration at the reactor feed leads to a reduction of total recycle quantity. From this would follow a reduction of total investment, of cooling water, and of energy plus the possibility of generating larger quantities of steam.

(*Brit. Chem. Engng.*, 13 (11), 1517)

[Original reference, *Verfahrenstechnik* 8 (1968) 335]

ESSO Urea Process

ESSO Research and Engineering Co., Del has developed a process for urea synthesis (U. K. Patent 1,106,024) in which the reactor and carbamate decomposition/stripping sections are integrated into a single unit, so that maximum use is made of the heat produced by the urea formation in the stripping system which follows. In this way, equipment, like pumps, compressors and heat exchangers, are minimized.

In this process, the usual synthesis reac-

tion of ammonia with carbon dioxide takes place at 100 to 300 atm. and at 140 to 200°C with a residence time of between 5 and 60 minutes. Liquid ammonia feed is introduced through a sparger at the bottom of the reactor. Simultaneously, a stream of cool petroleum oil of lower density than the urea melt produced in the reactor (i.e. specific gravity about 0.75 to 0.90) is introduced through the riser by a bubble-cap. This oil serves to partially control the temperature of the reactor, the remainder of the cooling being achieved by the steam generating coil fitted into the reactor wall.

The oil disperses itself in the urea melt which contains urea, ammonium carbamate and water and this mixture eventually passes down the downcomer into the decomposer/stripper section, where carbamate is stripped as gaseous NH_3 and CO_2 at 5 to 15 psi. from the urea solution by an upward current of carbon dioxide. In this way the stripped gases, together with the excess carbon dioxide stripper, flow upwards through the column, eventually passing through bubble-caps into the reaction zone, where the CO_2 -rich gas mixture is reacted with the ammonia feed. The hydrocarbon oil supplies the heat necessary for the decomposition and thus becomes cool again.

The melt, which now contains stripped urea and oil, next passes through a coalescing section packed with Teflon Raschig Rings, and hence the urea and oil separate into two layers. Cool oil is recycled into the reactor through the riser, at a rate controlled by the level device and the stripped urea is tapped off at a rate controlled by the level device.

Small quantities of water, carbon dioxide and ammonia, together with slight amounts of biuret, are present in the stripped urea product, which is subsequently degassed by simple flashing and crystallized. Mother liquor obtained during crystallization may be recycled to the top of the reactor, to scrub ammonia and carbon dioxide from the reactor gases before they are vented.

In this essentially once-through process, the $\text{NH}_3:\text{CO}_2$ mole ratio is about 2:1, and when operating at 180°C and at 150 atm, about 40 mm. Btu/hr of heat is released by the synthesis reaction, of which 25 mm. Btu/hr is absorbed by the oil. The remainder of this heat (15 mm. Btu/hr) may be used to generate steam in the water coil.

[*Nitrogen*, No. 55, (1968), 43]

Resources for Ammonia Production in India

In India the first fertilizer factory was based on electrolysis of water in Mysore due to cheap hydro-electric power. The second plant was based on gasification of wood at Alwaye, now converted to oil gasification. The three coal-based plants are at Sindri, Rourkela and Neyveli. While the Rourkela plant is based on the principle of supplying metallurgical coke to steel industry and using the by-product coke oven gas for ammonia synthesis, the Neyveli plant is based on direct gasification.

Meanwhile, process developments took place in USA, UK etc. to utilize lighter fraction for production of petrochemicals of which ammonia is a major item. The increasing cost of coal in UK and the increasing demand for fuel oil and middle distillates for railway traction and public roadways led to the surplus production of naphtha. So the next several fertilizer projects veered towards petroleum industry.

But with the sanction of several naphtha-based ammonia plants, a naphtha-crisis is now envisaged for fertilizer production. There are many who even advocate import of ammonia. In a paper* presented at a seminar of the Mining, Geological and Metallurgical Institute at Calcutta, D. Mukherjee, M. M. Sen and A. Lahiri of Central Fuel Research Institute, Dhanbad (Bihar) have very ably advanced the case of coal as a permanent and long-term source for production of fertilizer and energy in India. They have evaluated the problems for production of fertilizer from coal. Even if it is found that production of fertilizer based on coal is costlier, there is enough justification, both from strategy and national need, for investment in production of fertilizer based on coal as a long-term solution. Using coal, much of the equipment for coal-based fertilizer industry can be made within the country with far less dependence on technical know-how from abroad, and a similar independence in the matter of raw materials, catalyst, equipment spares and in operating skill is also possible.

Among the processes for production of hydrogen studied (Table 1), the authors claim that the production cost of hydrogen by direct gasification of coal is barely 25-30 per cent higher even in the worst case above the same based on naphtha. Moreover, the

cost of delivered naphtha is taken as Rs. 130/ton which may be higher for plants located away from the source of naphtha. At higher prices of naphtha, the cost of production of hydrogen from coal-based plants in spite of higher capital investment in them will be competitive if not cheaper.

Fertilizer plants based on coal should be located near mines and if integrated with power generation the cost will be even lower. When urea is the ultimate objective, pure carbon dioxide produced in course of shift reaction and gas purification has a special significance. Further, in the coal gasification process (Table 1), the extra steam required for the process is assumed to be obtained from external sources though this may not be the case always. According to the authors, for ammonia plants based on production of hydrogen by coal gasification to be competitive with those based on naphtha, the following conditions should be satisfied: (i) coal supply should be cheap (ii) transport of coal from the mine should be avoided (iii) base-load power from pit-head power generation units should be made available, and (iv) the capacity of ammonia plants should be such that speci-

fic power consumption for oxygen generation is minimum i.e. ammonia plants more than 600 tons/day should be planned. Additional economy will result from further integration, especially when the end-product is urea and when low pressure steam for the coal gasification is utilized.

As regards the steam-iron process, the U.S. Bureau of Mines have experimented with variations of the same reaction using fluidized-bed technique under pressure and the preliminary pilot plant data have indicated that hydrogen produced by this process will have the same cost as by the steam-naphtha reformation. As no oxygen plant will be required, so foreign exchange can be saved; moreover, hydrogen is produced under pressure and is more than 99 per cent pure which will accrue saving in the compression and purification of the gas.

The Institute of Gas Technology, Chicago, have also calculated the costs of production of hydrogen on the basis of a conceptual design of a steam-iron reaction plant under higher pressures (80 kg/cm²). Here the producer gas is generated at higher pressure and by-product power

TABLE 1—COST COMPARISON OF DIFFERENT PROCESSES FOR PRODUCTION OF HYDROGEN
(Capacity, 426 million Nm³ per year)

Sl. No.	Cost Item	Steam Re-forming of Naphtha	Pressure Gasification of coal	Gasification of dust coal	Steam-iron process (Medium pressure)	Steam-iron process (High pressure)
1.	Erected plant cost	100	176	202	275	233
2.	Working capital	100	129	142	194	167
3.	Raw material cost ⁽¹⁾	100 ⁽²⁾	49	39	58 ⁽²⁾	43
4.	Other direct operating costs	100	292	331	123	160
5.	Indirect operating costs	100	173	198	269	228
6.	Cost of production of 1000 Nm ³ H ₂	100	128	136	—	—
7.	Cost of compression per 1000 Nm ³ H ₂ from purification exit pressure to 25 Kg./cm ²	100	33	33	—	—
8.	Cost of production of compressed H ₂ (96%)	100	123	130	102 ⁽³⁾	95 ⁽⁴⁾

Note—(1) Naphtha @Rs. 130/t. and coal @ Rs. 25/t; (2) includes fuel cost; (3) 99.8% pure hydrogen at 32 kg/cm²; and (4) 99.8% pure at 79 kg./cm².

*Resources for Production of Synthetic Ammonia for Fertilizer Industry.

is generated through the expansion of hot gases via gas turbing; and even with delivery of hydrogen at higher pressure and of high purity, the study indicates lower costs of hydrogen-making than by naphtha reforming.

Coming to the relative costs of production of ammonia, the authors, based on a comparative study of 3 processes, conclude that the modified pressure gasification of coal compares very well with naphtha reformation (Tables 2 & 3). In the existing pressure gasification process, carbon utilization is somewhat lower chiefly due to production of by-product tar; however, in successful pilot plant trials tar has been recycled in the gasifier and subsequent reformation of the raw gas with light tar for production of carbon monoxide and hydrogen has been achieved. With these modifications, the production costs of hydrogen, even excluding raw materials considerations, are comparable with naphtha reformation. Injection of additional petroleum feedstocks in such a system may further reduce costs of production of ammonia without adopting catalytic naphtha reforming technique. Costs of additional oxygen required for reformation are stated to be more than covered by by-products steam. The corresponding cost index for dust gasification process is slightly higher (Table 2) chiefly due to higher oxygen consumption but this technique, being flexible with regard to raw material, e.g. coals, oils or gas, and to the fact that such plants are easier to fabricate, operate and control, can also be considered, especially if oil support is given.

According to the authors, even at a low price of Rs. 90/ton of naphtha as feedstock

with fuel oil at Rs. 177/ton for supplying process heat, the cost of ammonia is only at par with the modified pressure gasification technique with coal price at Rs. 25/ton. If the cost of naphtha is taken at a reasonably higher, say Rs. 130/ton price, pressure gasification becomes cheaper even with coal price at Rs. 35/ton. At these prices even dust coal gasification process with coal price at Rs. 35/ton will be cheaper.

Allowing for a return of 10 per cent on capital cost, the modified pressure gasification process can produce ammonia at Rs. 388/ton with coal at Rs. 29/ton, compared to Rs. 416/ton for a naphtha-based plant with naphtha and fuel oil prices at Rs. 190 and Rs. 270/ton respectively. After amortization in 10 years, the coal-based processes will be far cheaper than a naphtha-based plant due to their lower cost of raw material requirements.

Production of coal-based ammonia will be more favourable if integrated with large coal-based complexes, e.g. with coke oven plants, manufacture of synthetic fuels, supply of town gas (with pressure gasification), etc. With increasing production of steel and construction of large merchant coke ovens, integration with ammonia manufacture could result in considerable lowering of costs in production of ammonia.

Production of fertilizers can be a major undertaking in a synthetic oil complex based on coal gasification and Fischer-Tropsch catalytic synthesis, as has been demonstrated at Sasolburg (S. Africa); but such an integrated project must be based on cheap coal as 5 tons of coal are required for a ton of synthetic condensates.

TABLE 3—TYPICAL RESULTS OF PRESSURE GASIFICATION OF TALCHER COAL

1. Gasifier pressure, Kg./cm ²	..	25
2. Size of coal charged, mm.	..	6-25
3. Dry coal feed rate, Kg./hr.	..	450
4. Oxygen/coal Nm ³ /kg.	..	0.284
5. Steam/coal, Kg./kg.	..	1.747
6. Gas make rate, Nm ³ /hr.	..	794
7. Gas produced/kg. of coal, Nm ³ .	..	1.764
8. Raw gas composition, % by vol.		
CO ₂	..	30.9
CnHm	..	0.8
O ₂	..	—
CO	..	17.2
H ₂	..	38.7
CH ₄	..	11.7
N ₂	..	0.7
9. Calorific value of raw gas (dry) kcal./Nm ³ .	..	2944
10. Yield of tar/ton of dry coal, litres.	..	57.5
11. Cold gas efficiency, %	..	74.4
12. Carbon gasified, %	..	82.8

(Source—Report on Gasification Tests with Talcher Coal (CFRI 1966).

The tail gases and the lighter fractions from F.T. process are excellent sources for synthesis of ammonia and can utilize all the advantage of low investment costs of naphtha-based plants.

Hydrogenation of coal can also be integrated with fertilizer industry as the former will produce not only by-product ammonia but also tail gases which can be profitably converted to fertilizer. Since such synthetic oil plants must necessarily have a high capacity (not less than 50,000 barrels/day), very large quantities of fertilizer can indeed be produced from by-product gases and from by-product ammonia produced. Assam coals, if hydrogenated, will liberate sulphur, which can be either marketed as such or converted to ammonium sulphate, since tail gases in such cases will be under high pressure, there will be a corresponding reduction in compression costs for ammonia synthesis gas.

[FRI News, 18 (1968), 52].

TABLE 2—COST COMPARISON OF THE DIFFERENT PROCESSES FOR AMMONIA PRODUCTION

Sl. No.	Cost item	Steam reforming of Naphtha	Pressure Gasification of coal (modified)	Gasification of dust coal
1.	Erected plant	100	157	183
2.	Working capital	100	137	158
3.	Direct operating cost, excluding raw material for process	100	75	84
4.	Indirect operating costs	100	156	174
5.	Cost of production of ammonia excluding raw material for process	100	101	120

News in Brief

Naphtha Reformation Unit at Rourkela

The naphtha unit of Hindusthan Steel's Fertilizer Plant at Rourkela was formally inaugurated on Jan. 21, 1969. This unit, built in collaboration with Dr. C. Otto of Bochum, will not only increase the output of fertilizer but change the financial position of the adjoining steel plant also.

[*Chem. Age of India*, 20 (1) (1969), 8]

Proteins from Petroleum

For the first time in India, Gujarat refinery near Baroda is to start production of proteins from petroleum on a commercial basis as Ankleswar and Kalol crudes with high paraffin content have been found to be more suitable. A French pilot plant with a production capacity of about 50 kg. of protein concentrate daily using gas oil as the starting material will go into operation in early 1969. This plant is at present in operation at IIP, Dehra Dun.

The plant mainly consists of a one cubic metre capacity fermenter and treatment unit to produce an odourless and tasteless powder. The paraffinic hydrocarbon is thus treated by means of micro-organisms, yeast in presence of air and aqueous solution containing nitrogen, phosphorus, potassium, etc. essential to living organisms.

A suitable method has also been developed by IIP to treat the cream obtained from fermentation with a view to get pure protein-concentrate without any residual hydrocarbon. A ton of gas oil when treated in this process yields about 0.2 tonne of protein concentrate with 50 per cent of high nutrition value.

[*Oil Commentary*, 6 (9-11), (1969), 24]

Sale for Fertilizers by Public Sector Plants

Public sector fertilizer plants were, with effect from Oct. 1, 1967, to sell 50% of the fertilizers in the open market. This limit was raised to 100% from Oct. 1, 1968 with an option to the Government to buy 30% of the total production at a negotiated price.

(Source: Lok Sabha, Dec. 9, 1968)
(ibid)

ONGC Research Institute

One million dollar aid has been received from the U.N. Development Programme by the Oil & Natural Gas Commission for its research and training institute at Dehra Dun. The aid was to be used for meeting the expenditure of the services of U.N. experts, procurement of equipment and training of personnel abroad. The Government of India was to make a counterpart contribution in rupees, equivalent to U.S. \$ 983,900 to meet the expenditure on the services of Indian personnel. The major programmes pursued so far and being pursued at present are: basin studies for oil and gas prospects in selected area; drilling rate studies; designing of well-logging and seismic amplifier systems; petroleum source rock investigations; crude oil correlations; improvements of oil well cement quality; technological schemes for oil field development; water-injection studies for increasing oil recovery.

[*ibid*, 29]

FCI Exports

Fertilizer Corpn. of India Ltd., has in its first ever export venture despatched 100 tonnes of ammonium bicarbonate to Kuwait recently. It is used mainly as a leavening agent in bakeries. A preliminary market survey has shown that export potential for pharmaceutical grade ammonium bicarbonate is good in the Far East, West Asia, and African countries.

Target of Fertilizer Production

On the assumption that the fertilizer projects now under consideration will be

approved and implemented on schedule, the production of fertilizers (in million tonnes) is expected to be of the following order:

	Nitrogen	P ₂ O ₅
1971-72	1.935	0.816
1975-76	5.076	2.485
1978-79	6.626	3.345

The demand at present envisaged for the corresponding years is as follows:

	Nitrogen	P ₂ O ₅
1971-72	2.78	1.2
1975-76	5.00	2.5
1978-79	6.635	3.31

(*Oil Commentary*, 6 (9-11) (1969), 23]

Availability of Naphtha

A shortage of naphtha is likely to occur after 1971. As naphtha forms part of the light distillation fraction, a separate figure for naphtha cannot be given. The estimates of production and consumption (in million tonnes) of light distillates, including naphtha, during 1968 and the next five years and the consumption of naphtha only are as given in the Table below.

The consumption of naphtha in the existing fertilizer factories during 1968 will be about 220,000 tonnes, and to overcome its shortage alternative feedstocks, such as LSHS, coal, natural gas and imported ammonia, will be used. The question of maximizing the indigenous production of naphtha is being examined. The scope of basing some of the future petrochemical capacity on coal, fuel oil and natural gas to the maximum extent is being studied. Fuel oil can be used in place of naphtha for

	Production L. Distillates	Consumption of L. Distillates	Consumption of Naphtha
1968	2.640	1.900	0.456
1969	3.100	2.354	0.874
1970	3.589	3.083	1.514
1971	3.856	3.816	2.336
1972	4.322	4.756	3.186
1973	4.714	5.721	4.061

fertilizer production. This country is self-sufficient in fuel gas and will continue to be so. But the use of fuel oil as a feedstock to the extent feasible has to be justified on techno-economic considerations.

[*ibid*, 22]

Stabilizing Ammonium Nitrate

Ammonium nitrate undergoes volume expansion and contraction as it passes through its crystal transition temperatures, causing prills and granules to break down into fine particles or dust. The effect of various chemical additives on the physical breakdown at the transition temperatures has been studied. A mixture of boric acid, diammonium phosphate and ammonium sulphate has been found to be the most effective for stabilizing ammonium nitrate against physical breakdown as ammonium nitrate cycles through its transition temperatures. A commercially proven process has been developed for producing greatly improved granular and prilled ammonium nitrate, and mixed fertilizers containing ammonium nitrate.

(Brown, Marion L., Green, Albert W., and Blanton, Ladelle, Mississippi Chemical Corp., Yazoo City, Miss. Chem. Soc. Meeting, Chicago, Ill., September 1967)

[*The World of NPKS*, No. 28, (1968), 25]

Liquid Mixed Fertilizers

Describing the technology and economics of liquid fertilizers, Dr. T. P. S. Hignett, Director of Chemical Development, T.V.A., places special emphasis on phosphatic materials used in the mixture. Liquid mixed fertilizers which contain at least two of the three primary nutrients N, P_2O_5 and K_2O include true solutions, suspensions and slurries. Liquid fertilizers are getting more and more popular in America and in 1967 their use was about 22% of the total forms of all fertilizers. The most important convenience of liquid mixed fertilizer is trouble-free, labour saving, mechanical handling and application. Farmers often prefer liquid fertilizers for starter application. When the seed is being sown or planted the liquid is applied. The manufacturing operations are generally simple and economical and losses during manufacture are negligible. The cost of phosphatic component of liquid mixed fertilizer is somewhat higher than for solids. Fine potash used in liquids is less expensive than granular potash used in blends. But the

main disadvantage of the liquid mixed fertilizers is low analysis. There is low solubility of potassium chloride in liquid mixtures. In order to minimize the disadvantage of low analysis, the final product is transported only short distances from local mixing plants. Recent estimates indicate that clear liquids were slightly more expensive and suspensions slightly cheaper than bulk blends. Cold mix process is economically preferable to the hot mix plants of about 3000 tons/year output.

[*The World of NPKS*, No. 28, (1968), 10]

Caprolactum Plant

The Gujarat State Fertilizer Co. Ltd., is setting up a Rs. 22 crores caprolactum plant with technical collaboration of Inventa of Zurich and Ube Industries of Japan. The plant, when completed, will produce annually 20,000 tonnes of caprolactum, 24,000 tonnes cyclohexane, 84,000 tonnes of ammonium sulphate, 2,600 tonnes of soda ash and several other by-products in small quantities.

[*Oil Statistics*, 6 (3) (1968), 20]

Hydrogen Production

A new process for manufacturing pure hydrogen has been developed by the Pintsch Bamag A.G. from sulphur-free light distillate, liquefied petroleum gas or natural gas. It is mixed with steam at 25-30 atm, and catalytically reformed in an externally heated tubular reactor. The reformed gas is passed through a waste-heat boiler to raise the steam for the process. The carbon monoxide in the gas is then catalytically converted with steam to increase the hydrogen yield. After condensation of the excess steam, the gas is passed through diffusion cells containing palladium-silver membranes. The hydrogen diffusing through the membranes contains less than 1 ppm. of impurities and is absolutely dry. The residual gas is used for heating the reformer.

[*Fuel*, 47 (1968), 504]

Fertilizer Imports

Fertilizer imports during 1969-70 are likely to be of the order of 20 lakhs tonnes. Of this, nitrogenous fertilizers will account for 10.24 lakhs, phosphatic 4.19 lakhs and potassic 5.50 lakhs tonnes. Last year imports under these heads were around 17 lakhs tonnes. During the current year,

over 6.65 lakhs tonnes of fertilizers will be made available from various sources, viz. Poland (1 lakh te), USSR (2.5 lakhs te), Bulgaria (20,000 te), Rumania (25,000 te), Hungary (20,000 te), Japan (1 lakh te). Under barter deals 1.05 lakh tonnes would be obtained from Japan and U.S.A. Thus, the five E. European countries will be stepping up their exports to India from 3.80 to about 4.15 lakhs tonnes during the current year valued at about Rs. 30 crores which will result in foreign exchange saving.

[*FAI Inf. Serv.*, 10 (4) (1969), 6]

Indian Standards

Safety for Ammonia: ISI has published an Indian standard code of safety for ammonia (IS:4544-1968), which prescribes safety concerning hazards related to ammonia. It also describes the properties and essential information for safe handling and use of ammonia.

Ammonium Phosphate Sulphate Granular: ISI has prepared a draft standard specification for ammonium phosphate sulphate, granular [19.5—19.5—O Doc: CDC 24(3846)], which prescribes the requirements and methods of sampling test for the material. It is a complex fertilizer providing nitrogen and phosphorus to the soil. Its manufacture has started in India. The draft standard is being circulated for eliciting comments.

Urea Fertilizer Grade: A draft standard Doc: CDC 24(3435), which covers the requirements and methods of sampling and test for urea fertilizer grade, is being circulated by the ISI for eliciting comments. It is revision of IS: 1781—1961 which covered urea fertilizer and industrial grades. A separate draft standard for the industrial grade is under preparation.

[*Indian Chem. J.*, 3(2) (1968), 37 & 38]

Patents

Urea Synthesis Method: (Sumitomo Chemical Co. Ltd., Pat. No. 109945 Accepted on 15th July 1968.) Comprising reacting ammonia and carbon dioxide introduced to the first reaction zone kept 140-400 kg./cm² and at 160-230°C and then to the second zone which is maintained at the same or slightly lower pressure.

Methanol Synthesis Process: (Chemical Construction Corpr. Pat. No. 108892 Accepted on 11th July 1968.) Comprises catalytically reacting hydrogen and CO

at high pressure and temperature, heat exchanging, the hot gas mixture with a liquid under pressure. The methanol vapour thus cooled is condensed and separated and the liquid vapour is expanded through mechanical power recovering means, the usable power is utilized to recompress the cold vapour to a liquid for recycling.

Recovery of Phosphate Materials from Phosphate Rock: (Armour Agricultural Chem. Co. Pat. No. 112050 Accepted on 15th July 1968.) Introducing phosphate rock, nitric acid, ammonium bisulphate into digestion zone and separating insoluble calcium sulphate.

Separation and Recovery of Ammonia and Carbon Dioxide from an Ammoniacal Ammonium Carbonate Solution: (Osterreichische Stickstoffwerke Aktiengesellschaft. Pat. No. 110374 Accepted on 12th July 1968.) Comprises removing the bulk of free ammonia from the solution at atmospheric pressure in a stripping column, passing the solution containing ammonium carbonate and residual amounts of free ammonia from the sump to the heat of a second column and removing the bulk of CO_2 by fractional distillation with heating.

Stabilized Ammonium Nitrate Compositions & Their Production: (Mississippi Chemical Corpr. Pat. No. 109021 Accepted on 4th July 1968.) Comprises crystallizing the ammonium nitrate from a liquid mixture with at least 0.2—2.5 per cent of boric acid, an alkali metal salt thereof, an ammonium salt thereof, or a mixture thereof.

[*Indian Chem. J.*, 3(2) (1968), 39 & 40]

Fertilizers During IV Plan

Under the auspices of the Fertilizer Institute Division of the Fertilizer Association of India, Sri V. N. Kasturirangan, Chief Project Officer in the Ministry of Petroleum & Chemicals, Mines & Metals, delivered a lecture on March 24, 1969 at the India International Centre, New Delhi on "Fertilizer Scene—Fourth Plan", with Sri Satish Chandra, Chairman, FCI Ltd., presiding. The lecturer covered the present production and the future requirements of the various nitrogenous and phosphatic fertilizer during the fourth plan period. The normal feedstock for the nitrogenous fertilizer industry in India is naphtha, but in view of its anticipated shortage by 1970-71, alternate raw materials like LSHS and coal are considered for some of the projects. Process know-how for some of the fertilizers is indigenously available and it may be necessary to import partial or complete know-how for the rest. Considerable facilities are now available in public and private sectors for the design and engineering of fertilizer plants. Some of the catalysts needed for the industry are being developed indigenously and awaiting the commercial production and optimisation of their performance. One aspect which has to be planned well in advance is the training of personnel at all levels to take charge of the growing industry.

The occurrence of rock phosphate and pyrites close to each other in Rajasthan is an advantage as a distinct possibility exists for large scale production of phosphoric acid/ complex fertilizer, etc. The deposits

in Mussoorie (U.P.) are also being prospected, and it is hoped that after beneficiation these will furnish adequate phosphate for some of the plants. The smelter gases at Alwaye, Udaipur and Khetri do make a useful substitution in this regard in eliminating the use of sulphur.

Despite the recent excise levy, fertilizer costs in India are not as high as commonly made out to be, but these are undoubtedly higher than the international prices in absolute value but so are the food prices in the country. However, this argument does not take away the case for reduction of production cost of fertilizer so as to bring the input within the reach of the bulk of Indian farmers. A considerable improvement in this direction could be achieved if all plants are operating at or near their rated capacity; at present the fertilizer industry as a whole has been operating at about 60-65 per cent of its rated capacity.

Fertilizer Institute, Proceedings No. 2. (FAI, New Delhi), 1969.

Price of Natural Gas

The price of natural gas per cu. ft. supplied by Oil India to Namrup fertilizer plant is Rs. 42.10 per 1000 cu. metres. The prices charged from other consumers are as follows: Assam Oil Co. Rs. 17.54 (will be increased to Rs. 42.10 when FCI start taking gas); Assam State Electricity Board Rs. 8.77; Tingri and Moran gas grids & Nahorkatiya brickworks Rs. 52.62.

[*Oil Commentary*, 6(9-11) (1969), 21]

STATISTICS

TABLE 1—PRODUCTION OF FERTILIZERS IN INDIA DURING 1967-68, TONNE
[Prices (Rs/te) within brackets]

	Sindri	Nangal	Trombay	FACT (Udyogamandal)	Rourkela	Neyveli
Ammonium Sulphate	2,41,300 (492)	—	—	77,699 (495)	—	—
Ammonium Sulphate Nitrate	61,384 (577)	—	—	—	—	—
Urea	16,164 (840)	—	57,436 (840)	—	—	71,414 (800)
Calcium Ammonium Nitrate (20.5 % N)	—	1,43,597 (437)	—	—	1,89,503 (385)	—
Calcium Ammonium Nitrate (25 % N)	—	1,92,911 (510)	—	—	—	—
Nitrophosphate (16 : 13)	—	—	22,355 (863)	—	—	—
Ammonium Phosphate	—	—	—	55,881 (710)	—	—
Superphosphate	—	—	—	42,176 (312)	—	—
Suphala (20 : 20)	—	—	70,652 (890, reduced to 870 from 18-9-67)	—	—	—

[Oil Commentary, 6 (9-11) (1969), 23]

TABLE 2—CATALYSTS COMMERCIALY AVAILABLE FOR MODERN AMMONIA PLANTS

Service	Catalyst Composition	Form	Operating range temp.	Expected life under careful operating conditions	Remarks
Hydrodesulphurization	Cobalt Oxide 4 % Molybdenum 12 % on Alumina	Pellets Granules	260-430°C	3 to 5 years	
Desulphurization (Absorbent)	(1) Zinc Oxide plus Binder (2) Alkalized Iron Oxide (3) Metal Impregnated Carbon	Pellets Extrudates Crushed particles	200-350°C 400°C 400°C	18 % pick up 2 % pick up 1 year	
Primary Reformer	Naphtha Reforming 20 % Nickel Oxide on Ca, Mg, Si and Al Oxides with Potash Promoters Light Hydrocarbon Reforming 22-39 % Nickel Oxide on Re- fractory Carrier, plus Promoters	Rings, Pellets Irregular lumps	750-850°	3 years 5 years	
Secondary Reformer	18-21 % Nickel Oxide on Cal- cium Aluminate	Rings, Pellets, Spheres	982-1684°C	3 to 5 years	Two different layers of catalysts used. The one nearer to inlet is more temperature resistant
H. T. Shift	Chromia Promoted Iron Oxide Cr ₂ O ₃ 0-11 % Fe ₂ O ₃ 77-81 % Graphite 3-4 %	Pellets Tablets	300-575°C		
Methanation	Nickel Oxide 32 %-68 % Remaining Carrier Binder	Tablets	205-540°C	2 years	
Ammonia Synthesis	Promoted Magnetite	Granules	350-500°	4 years	

[Murthy, P. S., *Indian Chem. J.*, 3 (2) (1968), 71]

TABLE 3—CATALYST REQUIREMENTS FOR PRODUCTION OF AMMONIA

[Cost of catalyst at time of initial charge purchased, \$/daily ton of NH₃]

Year Built	1941	1952	1953	1957	1958	1961	1963	1964	1965	1968
Desulphurization	75	34	54	21	39	37	54	10	10	14
Primary Reforming	430	304	142	152	71	51	39	49	30	25
Secondary Reforming	965	—	351	126	85	76	61	31	32	41
CO-Conversion	870	672	383	230	240	174	126	159	185	121
Methanation	—	690	—	415	180	94	80	63	25	22
Totals	\$2,340	\$1,700	\$930	\$944	\$615	\$432	\$360	\$312	\$282	\$223

[Habermehl, R., *Indian Chem. J.*, 3 (2) (1968), 59]TABLE 4—CATALYST COSTS FOR A TYPICAL AMMONIA PLANT
[Catalyst Cost per daily ton of Ammonia, \$]

Year	1956	1958	1963	1964	1968
Desulphurization	62	54	54	50	41
Reforming	254	170	100	98	92
CO-Conversion	475	220	126	126	106
Methanation	213	142	80	72	48
Total	\$1,004	\$586	\$360	\$346	\$287

[Habermehl, R., *Indian Chem. J.*, 3 (2) (1968), 59]TABLE 5—STATE-WISE ANTICIPATED REQUIREMENT OF
FERTILIZERS (1973-74)

(thousand metric tons)

Sl. No.	State	Anticipated requirement by 1973-74		
		N	P ₂ O ₅	K ₂ O
1.	Andhra Pradesh	425.0	224.0	246.0
2.	Assam	62.0	35.0	26.0
3.	Bihar	324.0	140.0	96.0
4.	Gujarat	205.0	90.0	10.5
5.	Kerala	120.0	80.0	155.0
6.	Jammu & Kashmir	18.0	7.0	6.8
7.	Madhya Pradesh	170.0	115.0	2.8
8.	Madras	270.0	174.0	170.0
9.	Maharashtra	436.0	158.0	75.0
10.	Mysore	220.0	131.0	75.0
11.	Orissa	146.0	60.0	20.5
12.	Punjab	304.0	92.0	83.0
13.	Rajasthan	194.0	57.0	18.5
14.	Uttar Pradesh	590.0	247.0	15.1
15.	West Bengal	159.0	85.0	22.8
16.	Delhi	2.8	0.9	1.3
17.	Himachal Pradesh	4.4	1.6	0.6
18.	Tripura	4.0	2.6	3.0
19.	Manipur	0.8	0.3	0.1
20.	Plantations	75.0	34.6	77.0
		3,730.0	1,735.0	1,105.0

Complete target as worked out
by the Ministry of Food &
Agriculture

3,730.0 1,735.0 1,105.0

[Fertilizer Statistics 1967-68 (Fertilizer Assn.
of India, New Delhi), 1968, 184]

TABLE 6—AREA, PRODUCTION AND YIELD PER HECTARE OF PRINCIPAL CROPS (ALL-INDIA)

Crop 1	Area ('000 ha.)			Production ('000 tes.)			Yield per hectare (kgs.)		
	1964-65 2	1966-67* 3	1967-68* 4	1964-65 5	1966-67* 6	1967-68† 7	1964-65 8	1966-67 9	1967-68 10
Cereals									
Rice	36,364.0	35,250.8	36,721.8	39,034.2	30,437.9	37,858.1	1,073	863	1,031
Jowar	17,938.2	18,054.1	18,630.3	9,749.0	9,223.8	10,107.2	543	511	543
Bajra	11,725.8	12,239.6	12,539.2	4,453.9	4,468.3	5,131.9	380	365	409
Maize	4,618.0	5,073.8	5,576.7	4,658.1	4,893.6	6,275.1	1,009	964	1,125
Ragi	2,437.4	2,315.8	2,351.5	1,897.6	1,630.6	2,031.0	779	704	864
Small millets	4,512.6	4,584.0	4,755.7	1,952.5	1,488.5	1,911.9	433	325	402
Wheat	13,460.4	12,837.6	14,916.4	12,290.3	11,392.8	16,567.4	913	887	1,111
Barley	2,684.3	2,824.8	3,326.4	2,522.6	2,348.4	3,468.9	940	831	1,043
Total	93,740.7	93,180.5	98,818.0	76,558.2	65,883.9	83,351.5	817	707	843
Pulses									
Gram	8,895.7	8,003.2	8,236.5	5,785.2	3,622.0	6,042.3	650	453	734
Tur	2,495.6	2,521.0	2,680.9	1,887.8	1,129.7	1,734.9	756	448	647
Other Pulses	12,401.4	11,597.1	11,748.8	4,764.4	3,595.4	4,458.8	384	310	380
Total	23,792.7	22,121.3	22,666.2	12,437.4	8,347.1	12,236.0	523	377	540
Total Foodgrains	117,533.4	115,301.8	121,484.2	88,995.6	74,231.0	95,587.5	757	644	787
Oilseeds									
Groundnut (in shell)	7,216.3	7,299.1	7,553.6	5,887.7	4,410.9	5,829.1	816	604	772
Sesamum	2,512.7	2,793.4	2,686.6	492.8	416.0	421.4	196	149	157
Rapeseed & Mustard	2,881.3	3,005.9	3,204.0	1,466.4	1,227.9	1,481.9	509	408	463
Linseed	2,059.4	1,495.4	1,671.2	503.1	259.9	398.2	244	174	238
Castor	440.1	400.9	390.0	108.3	109.8	107.2	246	274	275
Total	15,109.8	14,994.7	15,505.4	8,458.3	6,424.5	8,237.8	560	428	531
Fibres									
Cotton (Lint)	8,271.4	7,835.7	8,046.8	5,663.8**	4,973.0**	5,562.3**	123	114	124
Jute	838.5	796.8	885.3	6,020.5**	5,357.9**	6,369.2**	1,292	1,210	1,295
Mesta	359.5	321.9	313.8	1,583.1**	1,220.8**	1,130.0**	793	683	648
Miscellaneous Crops									
Ginger (Dry)	21.9	22.6	22.3	20.8	21.2	20.4	950	940	915
Chillies (Dry)	717.1	721.0	759.8	469.1	418.2	486.5	654	580	640
Black pepper	102.3	102.2	102.3	24.0	23.0	22.7	235	225	222
Sugarcane (Gur)	2,561.8	2,301.3	2,036.9	12,031.2	9,501.0	9,959.3	4,696	4,129	4,889
Potatoes	430.7	473.3	504.0	3,667.9	3,521.5	4,233.2	8,516	7,440	8,399
Tobacco	394.3	423.5	397.6	345.6	353.4	344.0	876	834	865

*Partially revised estimates. †Final estimates.

**In thousand bales of 180 kgs. each.

[Indian Agriculture in Brief 9th Ed. (Directorate of Econ. & Statistics, Ministry of Food, Agric., CD & Coop., New Delhi), 1968, pp 82-85]

TABLE 7—ALL-INDIA LINEAR RATES OF GROWTH OF AGRICULTURAL PRODUCTION, AREA UNDER CROPS AND AGRICULTURAL PRODUCTIVITY FOR SELECTED CROPS AND GROUPS

Crop, Group 1	1949-50 to 1964-65 (Average: 1949-50 to 1951-52=100)			1952-53 to 1964-65 (Average: 1952-53 to 1954-55=100)		
	Production (per cent) 2	Area (per cent) 3	Productivity (per cent) 4	Production (per cent) 5	Area (per cent) 6	Productivity (per cent) 7
Rice	4.21	1.34	2.43	3.64	1.57	1.80
Jowar	2.98	0.97	1.74	1.99	0.40	1.57
Wheat	5.25	3.18	1.39	3.80	2.57	1.00
Foodgrains	3.66	1.48	1.80	2.75	1.02	1.60
Oilseeds	3.85	2.93	0.66	3.95	2.90	0.87
Sugarcane	5.57	3.68	1.36	7.83	4.93	1.93
Cotton	6.05	2.79	2.28	3.81	1.27	2.25
Non-Foodgrains	4.39	2.90	1.11	4.79	2.56	1.79
All Crops	3.92	1.72	1.78	3.42	1.28	1.91

[*Indian Agriculture in Brief*, 9th Ed. (Directorate of Economics & Statistics, Ministry of Food, Agriculture, C. D. & Cooperation, New Delhi), 1968]

TABLE 8—PRODUCTION OF NITROGENOUS FERTILIZERS IN INDIA

Year	Sulphate of Ammonia (20.6 %N)	Urea (46 %)	Ammonium Sulphate Nitrate (26 %N)	Calcium Ammonium Nitrate (20.5 %)	Ammonium Chloride (25 %N)	Ammonium Phosphate (16 %N)	Total in terms of Nitrogen
1951†	53,551	—	—	—	—	—	11,032
1956†	396,883	—	—	—	—	—	81,758
1961-62	403,627	13,635	55,427	200,779	17,826	14,112	151,704
1962-63	422,798	18,717	62,229	314,799	19,621	9,223	182,800
1963-64	440,358	18,115	47,211	493,837	19,631	28,674	222,050
1964-65	435,030	17,945	47,769	558,023	19,267	49,239	237,381
1965-66	420,231	27,547	55,255	496,732	22,537	52,121	232,031*
1966-67	437,490	131,874	60,018	538,716	22,574	77,694‡	307,936*
1967-68	—	—	—	—	—	—	367,000
1968-69 (Target)	—	—	—	—	—	—	650,000

*Includes production of Nitro Phosphate (16%) for the years 1965-66 (16,392 tonnes) and 1966-67 (70,608 tonnes).

†Calendar year.

‡Complex fertilizers containing both N and P.

[*Indian Agriculture in Brief*, 9th Ed. (Directorate of Econ. & Statistics, Ministry of Food, Agriculture, CD & Cooperation, New Delhi), 1968, 186]

TABLE 9—IMPORT OF NITROGENOUS, PHOSPHATIC POTASSIC, AND MIXED FERTILIZERS MADE FOR CENTRAL FERTILIZER POOL, TONNES

Year	Sulphate of Ammonia (20.6%N)**	Urea*	Ammonium Sulphate Nitrate (26%N)	Calcium Ammonium Nitrate (20%N)	Nitrophosphate (20%N) (20% P ₂ O ₅)	Ammonium Phosphate (20%N) (20% P ₂ O ₅)
1	2	3	4	5	6	7
19 1-52	142,247	—	—	—	—	—
1956-57	233,692	10,066	14,512	—	—	—
1961-62	293,975	129,683	29,076	61,785†	—	—
1962-63	670,900	219,340	—	—	20,238	30,563
1963-64	449,111	261,137	—	—	17,177@	48,840
1964-65	317,078	293,996	—	—	30,483	39,915
1965-66	852,820	251,927	—	—	—	62,442
1966-67	1,209,279	481,973	41,709	93,860‡	—	220,532
1967-68 (P)	1,048,170	918,367	16,070	125,055	—	256,458
Estimated Achievement						

@Here Nitrophosphate consists of 12.9% N and 12.9% P₂O₅.

†Here Calcium Ammonium Nitrate consists of 20.5%N.

**Upto 1960-61, the Nitrogenous content of Sulphate of Ammonia has been taken as 20.6% and for later years as 21%.

‡Here Calcium Ammonium Nitrate consists of 26% N.

*Upto 1960-61, the Nitrogenous content of urea has been taken as 45% and for later years as 46%.

TABLE 9 (Contd.) —IMPORTS OF NITROGENOUS, PHOSPHATIC, POTASSIC AND MIXED FERTILIZERS MADE FOR CENTRAL FERTILIZER POOL, TONNES

Year	Di-Ammonium Phosphate (18%N) (46% P ₂ O ₅)	Muriate of Potash (60% K ₂ O)	Ammonium Chloride (25%N)	Sulphate of Potash (48% K ₂ O)	Basic Slag (18% P ₂ O ₅)	NPK 14%N 14% P ₂ O ₅ 14% K ₂ O	Total in terms of		
	8	9	10	11	12	13	N	P ₂ O ₅	K ₂ O
1951-52	—	—	—	—	—	—	29,303	—	—
1956-57	—	205	—	—	—	—	56,443	—	123
1961-62	—	—	—	—	—	—	141,615	—	—
1962-63	—	—	—	—	—	—	251,946	10,160	—
1963-64	—	—	—	—	—	—	226,420	11,984	—
1964-65	—	—	—	—	—	—	213,740	11,915	—
1965-66	—	—	8,117	—	—	—	309,496	12,848	—
1966-67	230,202	—	21,203	4,985	2,013	—	617,000	150,362	143,000
1967-68 (P)	614,704	65,925	50,658	5,000	10,000	90,592	868,000	348,538	279,000
Estimated Achievement									

Note: Upto 1966-67, the figures have been taken from audited proforma accounts.

(P) Provisional.

[Indian Agriculture in Brief, 9th Ed. (Directorate of Econ. & Statistics, Ministry of Food, Agriculture, CD & Cooperation, New Delhi), 1968, 187-188 p]

TABLE 10—CONSUMPTION OF NITROGENOUS FERTILIZERS IN INDIA, TONNES

Year	Sulphate of Ammonia (20.6% N)	Urea*	Ammonium Sulphate Nitrate (26% N)	Calcium Ammonium Nitrate (20.5% N)	Nitrophosphate (20% N)	Ammonium Phosphate (20% N)	Total in terms of Nitrogen
1956-57	601,197	7,420	9,170	813	—	—	130,636
1961-62	669,491	113,596	79,896	149,349	—	4,115	242,405
1962-63	833,737	154,375	53,746	134,915	33	4,524	305,805
1963-64	984,341	214,188	51,924	408,718	1,263	2,974	399,354
1964-65	1,015,104	342,944	62,397	671,518	36,170	64,116	538,274
1965-66	1,183,029	312,052	46,493	592,262	84,625	6,338	540,803†
1966-67 (P)	1,581,674	586,812	86,805	507,261	61,170‡	19,586	856,533@

*Upto 1960-61 the nitrogenous content of urea has been taken as 45% and for later years as 46%.

@Includes consumption of (i) Calcium Ammonium Nitrate (22% N) 22,711 tonnes. (ii) Calcium Ammonium Nitrate (26% N) 75,273 tonnes. (iii) Ammonium Chloride (25% N) 34,787 tonnes. (iv) Chilean Nitrate (16% N) 120 tonnes. (v) Ammonium Phosphate (16% N) 76,020 tonnes, (vi) Diam Phosphate (18% N) 1,61,889 tonnes.

†Here Nitrogen content of Sulphate of Ammonia has been taken as 21%.

‡Here Nitrogen content of Nitro-phosphate has been taken as 16%.

(P) The figures are based on despatches made during the year and are provisional. These include, besides pool fertilizers, the quantities sold directly by the indigenous firms.

Notes:— (i) Some quantities of Ammonium Phosphate, Nitro-phosphate, Ammonium Nitrate etc. were imported during the last few years, in regard to which consumption statistics have not been furnished by the states.

(ii) Consumption figures upto 1965-66 pertain to the fertilizers handled by Pool.

[*Indian Agriculture in Brief*, 9th Ed. (Directorate of Econ. & Statistics, Ministry of Food, Agriculture, CD & Cooperation, New Delhi), 1968, 189]

TABLE 11—NAPHTHA DEMAND FOR PETRO-CHEMICALS

(Figures in '000 tonnes)

Supply Area	Plant	1968	1969	1970	1971	1972	1973	1974	1975
Assam		—	—	—	—	—	—	—	—
Barauni	Aromatics	—	—	—	—	—	80	100	120
	Sub-Total	—	—	—	—	—	80	100	120
Haldia	Olefine Complex	—	—	—	—	—	—	—	200
	Methanol	—	—	—	—	20	40	50	50
	Sub-Total	—	—	—	—	20	40	50	250
North-West		—	—	—	—	—	—	—	—
Kandia (MG)		—	—	—	—	—	—	—	—
Okha		—	—	—	—	—	—	—	—
Koyali (BG)	PVC (Kotah)	—	—	10	40	40	40	60	60
	Aromatics	—	65	83	134	134	134	134	134
	Naphtha Cracker	—	—	—	60	280	360	360	360
	Sub-Total	—	65	93	234	454	534	554	554
Bombay/Goa	UCIL	70	70	70	100	100	100	130	130
	NOCIL	130	180	225	225	240	300	300	300
	Methanol (Trombay)	30	30	30	40	40	40	40	40
	Calico (PVC)	—	—	10	30	30	30	50	50
	Sub-Total	230	280	335	395	410	470	520	520
Cochin	PVC (Tuticorin)	—	—	10	15	15	20	20	25
	Total	230	345	438	644	899	1,144	1,244	1,469

[Indian Petroleum and Chemicals Statistics 1967, (Economics & Statistics Division, Ministry of Petroleum & Chemicals, Govt. of India, New Delhi), 1969, 110]

TABLE 12—TARGETS OF FERTILIZER PRODUCTION & CONSUMPTION

Item	Unit	1960-61 Actuals	1965-66 Actuals	1968-69 Estimated	1973-74 target/ Estimates
1	2	3	4	5	6
<i>Fertiliser production</i>					
Nitrogenous (N)	Thou. tonnes	101	232	550	3,000
Phosphatic (P ₂ O ₅)	Thou. tonnes	53	123	220	1,500
<i>Consumption of fertilizers</i>					
Nitrogenous (N)	Thou. tonnes	210	550	1,400	3,700
Phosphatic (P ₂ O ₅)	Thou. tonnes	70	130	400	1,800
Potassic (K ₂ O)	Thou. tonnes	26	80	180	1,100
Plant Protection (area covered)	Mill. hectares	6.5	16.6	54	80

Source: Lok Sabha

[Hindustan Times, New Delhi, 23.4.69]

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EDITOR'S NOTE

It has been decided to publish in TECHNOLOGY research papers from scientists and technologists outside FCI Ltd. provided these are:

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An efficient method has been developed for measuring and controlling the thickness of thin sheets of any material utilizing the combined effect of absorption and backscattering of beta particles emitted from a $\text{Sr}^{90}/\text{Y}^{90}$ source. It has been shown that the resolving power of the process is higher than that obtainable by the earlier methods based on individual effects of absorption or backscattering of beta particles. This paper also describes the adjustment of several parameters to suit the particular range and sensitivity requirements.

Measurement and Control of Thickness by the Combined Effect of Absorption and Backscattering of Beta Rays

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Introduction

Radioisotopes have been used widely now-a-days in different types of measuring and controlling equipments. Various types of thickness-measuring gauges employing radioactive sources, which are in use so far, may be classified broadly into two groups—one using the absorption and other the backscattering of beta particles or gamma rays. Beta gauges are specially used for measuring and controlling thicknesses of thin sheets.

Beta particles emitted in radioactive decay process interact with both the electrons and nuclei of matter. These interactions may be elastic or inelastic. In elastic collisions, beta particles do not lose any energy but they are scattered undergoing sharp changes in direction. In inelastic collisions, these particles collide with the extra nuclear electrons and energy is lost in producing ionization. Moreover, the interaction of beta particles with the strong electric field surrounding the nuclei gives rise to the emission of electromagnetic radiations or bremsstrahlung. The loss of energy by this process is referred as radiation loss. The penetration of beta particles into matter depends mainly on the magnitude of energy losses by these two processes. In practice, the radiation loss is appreciable if the interaction occurs with high Z (atomic number) materials, viz. lead, tungsten, etc., and it is less important in the case of low Z materials like carbon, aluminium, etc. In passing through a substance, a beam of beta particles gets attenuated obeying the exponential absorption equation

$$I = I_0 e^{-\mu_m x} \quad \dots \quad (1),$$

where I is the intensity of emergent beam, I_0 the intensity of incident beam, μ_m the mass absorption co-efficient and x the thickness of absorber in terms of face density and is expressed in g./cm^2 . The thickness is, therefore, practically independent of the material of the absorber. Equation (1) gives the relation between the thickness of the absorber x and the intensity of beta radiations I and forms the basis of absorption gauges for thickness measurement.

The scattering of beta particles is a complex process and has been described in details by Schonland and Crowther¹. The beam of backscattered beta radiations consists of particles which have been deviated sufficiently to emerge from the scatterer in the opposite direction to which they entered. While passing through a medium the angular distribution of these particles is fairly of Gaussian type. For a definite geometry and source, the intensity of radiation backscattered from a thin sheet of parallel faces depends mainly upon two parameters, viz., the thickness and atomic number of the scattering material. With increase of thickness of the scatterer, the number of backscattered beta particles also increases and ultimately reaches a saturation value, corresponding to the plate thickness equal to 1/5th of the maximum range of beta particles emitted by the source into the material of the plate². It has been found to the extent of first approximation that the number of backscattered

beta particles at saturation is proportional to $\sqrt{Z}$. The intensity of direct radiation $I_{dir.}$ may be connected to that of backscattered radiation $I_{scat.}$ by the relation

$$I_{scat.} = K_{scat.} I_{dir.} \quad \dots \quad (2),$$

where $K_{scat.}$ is the backscattering co-efficient defined by the empirical relationship³

$$K_{scat.} = (0.0415Z^{\rho} - 0.4) \sin \phi_{scat.} + 0.4 \dots (3),$$

where $\rho \approx 2/3$ and $\phi_{scat.}$ is the scattering angle. The variation of the intensity of backscattered radiation with the thickness of the material x is given by

$$I_{scat.}(x) = I_{scat.} (1 - e^{-kx}) \dots (4),$$

where $I_{scat.}$ is the intensity of backscattered radiation from a body of thickness $x \gg x_{satd.}$ and is defined by the expression (2) and k is a constant co-efficient which depends on the energy E as³

$$k = \frac{40}{E_{max}^{3/2}} \left(\frac{cm^2}{gm.} \right) \dots (5).$$

The relation (4) is the mathematical basis for the construction of thickness gauges utilizing backscattering of beta rays.

The earlier gauges for the measurement and control of thickness of thin sheets utilized either, absorption⁴⁻⁶, or back scattering^{2,7} of beta particles using Ionization chambers or G.M. tubes as measuring or controlling devices. In the present method, the absorption and backscattering are taken up together and a thickness measuring and controlling gauge has been developed with an assembly of G.M. tubes, counting-rate meters and Sr^{90}/Y^{90} beta source. This device has been found more efficient than the methods based on either absorption or backscattering separately. The results obtained by all these methods are compared and shown in Table 1, which indicates clearly that the resolving power is far greater in the present process.

Experimental

The essential features of the experimental set-up are shown in Figs. 1 and 2. Two organic quenched end-window G.M. tubes, having mica window of thickness 1.5 mg/cm^2 , were used in conjunction with two linear count-rate meters with pulse shaping and diode pump circuits. Each count-rate meter was capable of counting upto 10^4 counts/sec. in full-scale deflection with an

integral time constant variable from 0.5 to 85 sec. in 5 steps.

One millicurie Sr^{90}/Y^{90} source was used as a beta emitter. For absorption studies the source was deposited in a stainless steel capsule of 1.5 cm. diam. and 2 mm. height having a 2mm. diam. drilled hole 1 cm. deep. The beam of beta particles was collimated properly to get the best results by means of annular lead rings. A similar source for backscattering was deposited in circular groove of thickness and depth 2 mm each in a stainless steel annular ring of inner and outer diam. 2.5 and 4cm. and thickness 1 cm. The sources, G.M. tubes, collimating assemblies, etc. were arranged over thick perspex mounts. The absorption set-up, including G.M. tube 1, source 1 and collimating assembly, were properly screened from the backscattering set-up including G.M. tube 2, and source 2, etc., (Fig. 1) by means of a suitable mild steel sheet.

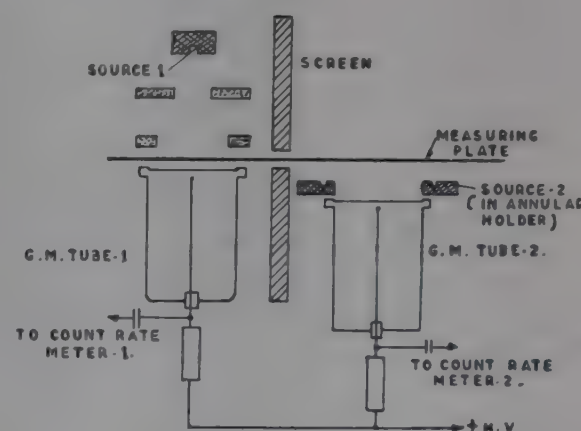


Fig. 1—G. M. Tube and Source Assembly

Experiments were performed only with aluminium sheet as an absorber and scatterer, which can similarly be extended for other materials. For calibration purposes, standard aluminium absorbers—also used as scatterers—covering the range 0 to 250 mg/cm^2 , obtained from Bhabha Atomic Research Centre, Trombay, were used. G.M. tubes and the sources were arranged in such a way that the best feasible geometry was obtained in the set-up.

In studying the absorption and backscattering combined process, G.M. tubes 1 and 2 were connected to the linear count-rate meters 1 and 2 respectively (Fig. 2). Besides the meters C_1 and C_2 , which measure the count-rates, one voltmeter V of suitable range and sensitivity was also connected across the diode pump circuits of the two count-rate meters through their cathode followers K_1 and K_2 . Evidently the voltmeter V would record the voltage difference developed across the cathode followers. This voltage could be set to a desired value by means of two potentiometers, P_1 and P_2 .

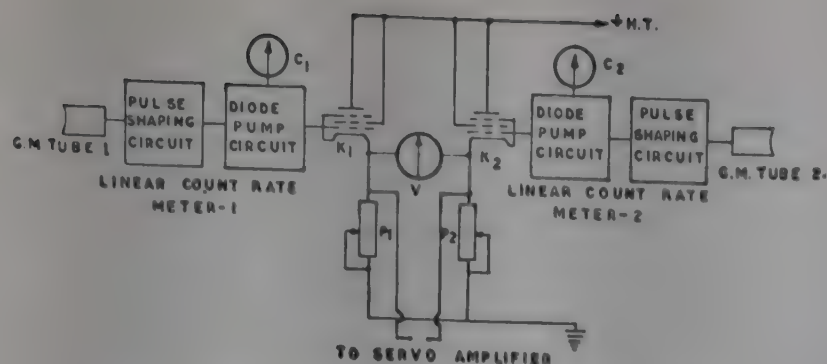


Fig. 2—Block circuit for Count Rate Meter

For any particular thickness of the sheet under measurement, voltages developed across cathode followers will be proportional to the counts obtained by the two G.M. tubes. These counts will alter with any change in thickness of the sheet in the opposite way. For example, if the thickness of the sheet increases, the count in G.M. tube 1 will decrease (absorption effect) and that in G.M. tube 2 will increase (backscattering effect). Similar changes in voltage will also be necessarily obtained at the cathode followers K_1 and K_2 respectively. The voltmeter will then get the addition effect of the small change of voltages across K_1 and K_2 and will give relatively large deflection. To make it clear, let the voltages developed across K_1 and K_2 be v_1 and v_2 respectively for a particular thickness of the sheet, so that difference of the voltage across V is $v_2 - v_1$ (say). With a small increase in the thickness of the sheet, the voltages at K_1 and K_2 change to, say, $v_1 - dv_1$ (absorption) and $v_2 + dv_2$ (backscattering) respectively. Therefore, the voltage across V will now be $(v_2 + dv_2) - (v_1 - dv_1) = (v_2 - v_1) + (dv_2 + dv_1)$. So the net change in voltage across V is $dv_2 + dv_1$. This shows that changes due to voltage in backscattering and absorption are additive giving a relatively large deflection in V than that obtained in any one of these processes taken up individually. This voltage in V plotted graphically against different known thicknesses of the measuring material gives the calibration curve and is used for the measurement of the unknown thickness. Thus, the scale of V in volts may be converted in 'thickness' after proper calibration.

Results and Discussion

For the measurement of thickness, calibration curves were first plotted between the count-rates vs. known thickness of aluminium (0 to 250 mg/cm²). Fig. 3 shows the absorption curve, where count-rates are obtained from the meter C_1 .

Fig. 4 shows the backscattering curve corresponding to the count-rates measured by C_2 . In the present absorption and backscattering combined process, count-rates

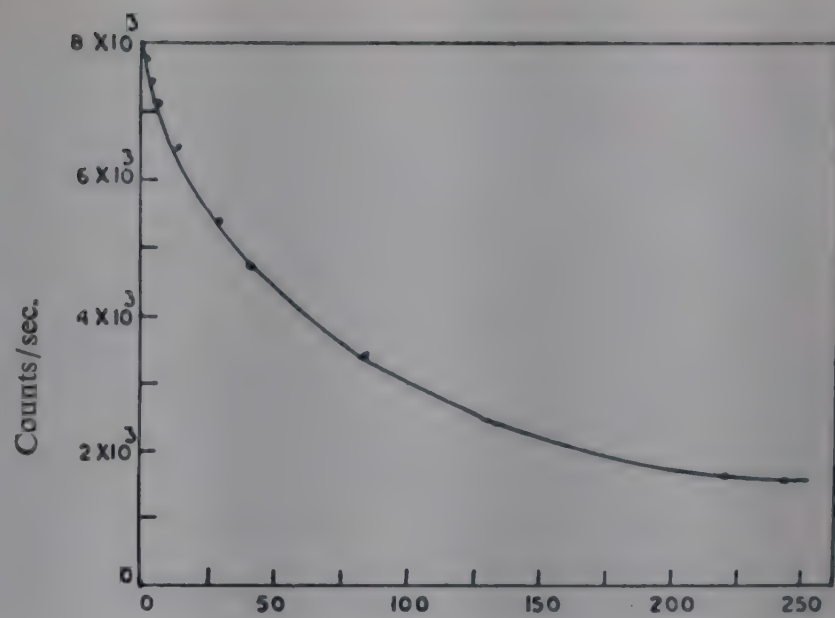


Fig. 3—Absorption Curve of Sr.⁹⁰/Y⁹⁰ Beta Radiation

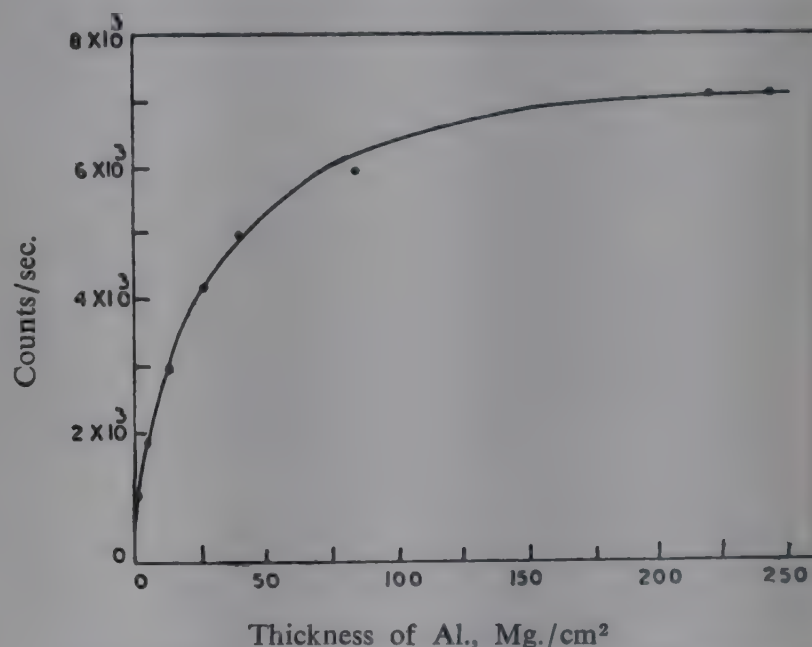


Fig. 4—Curve of Sr.⁹⁰/Y⁹⁰ Backscattered Beta Radiation

were noted simultaneously from the meters C_1 and C_2 , and the corresponding voltage difference across the cathode followers K_1 and K_2 was recorded by the voltmeter V for each known thickness of aluminium as absorber and scatterer.

The calibration curve, thus obtained, is shown in Fig. 5. Different calibration curves may similarly be obtained from different materials. In fact, voltmeter readings are sufficient for calibration purpose. But readings in C_1 and C_2 were also taken just to compare the efficiency of this method over that of the other two, because only count-rate meters were used for absorption and backscattering processes taken individually. The curves (Figs. 3, 4 and 5) were used for the measurement of unknown thicknesses by corresponding methods.

The efficiencies of the above three methods are compared in terms of their resolving power (R.P.), which

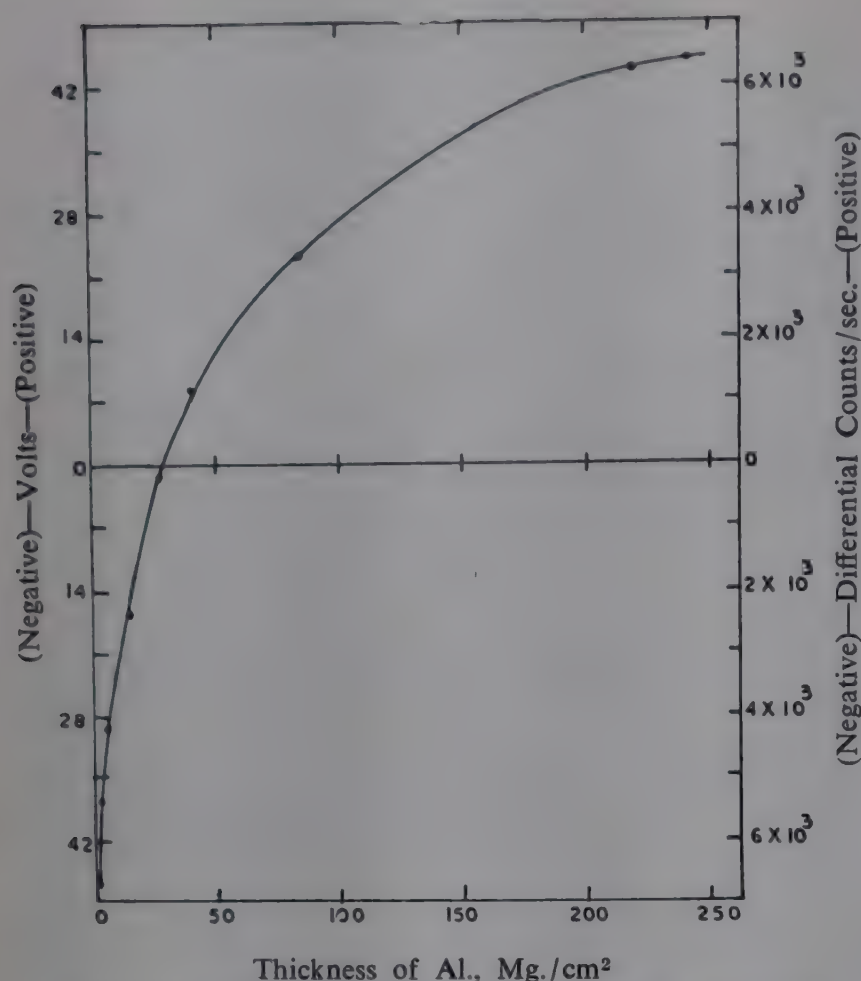


Fig. 5—Resultant curve of $\text{Sr}^{90}/\text{Y}^{90}$ Beta Backscattering and Absorption combined process. Positive and negative voltages correspond to the opposite sided deflection of the voltmeter with reference to 'Zero Point' of its scale. Differential count rate have been plotted by subtracting Absorption count rate from Backscattered count rate.

may be defined as a ratio of the output variation to the variation of the quantity to be measured, i.e. R.P.

$$= \frac{dI}{dx}, \text{ where } dI \text{ is the change in the beta flux measured}$$

by the counters corresponding to change in thickness dx of the absorber or scatterer. A comparison of resolving powers of the three methods actually obtained from Figs. 3-5 is shown in Table 1, over different thickness ranges for a change of $\pm 5 \text{ mg./cm}^2$.

TABLE I—RELATIVE RATIO OF RESOLVING POWERS OF THE THREE METHODS AT DIFFERENT THICKNESSES

Thickness of Al, mg./cm ²	Relative Ratio of Resolving Powers		
	By Absorption Method	By Backscattering Method	By Absorption and Backscattering Combined Method
25 ± 5	6	8	13.5
75 ± 5	2	2.5	4.2
125 ± 5	1.5	1	2.5

It is clear from the results (Table 1) that the resolving power is very high in the present process, as compared to the other processes.

It may be seen that the method may be adopted to control any desired thickness of a sheet under manufacture by using servo mechanism. The input of the servo-amplifier can be connected to the cathode followers K_1 and K_2 . The output of the servo-amplifier can be fed to a servo-motor, which in turn would control the thickness of the sheet. For this purpose, the deflection in voltmeter V is first made zero by equalizing the voltages in K_1 and K_2 . This is done by making count-rates in the ratemeters equal by adjusting the intensity of beta particles. The condition may be achieved by placing suitable fixed absorbers over the sources. Any finer adjustments necessary to make deflection in V zero can be done by potentiometers P_1 and P_2 . If there is a change in thickness of the sheet over the desired value it will develop a 'control voltage' across V . This voltage can be utilized through a servo amplifier to run a servo-motor for controlling the thickness. For plates of different thicknesses, the necessary zero shifting of the voltmeter to proper thickness regions may be done by placing suitable fixed absorbers over the sources, as

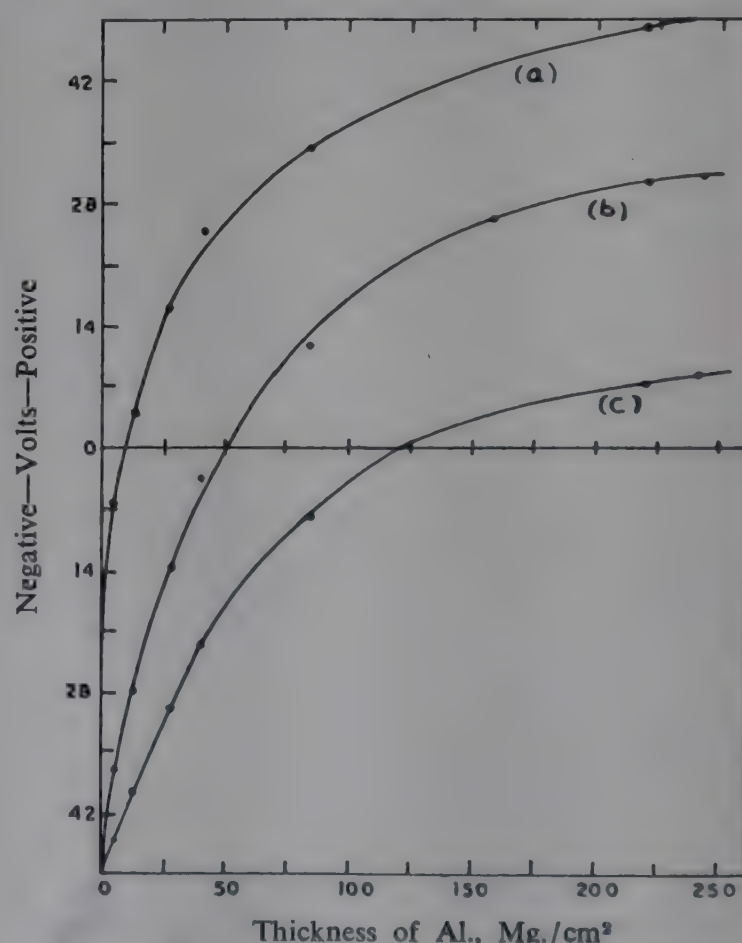


Fig. 6—Resultant curve of $\text{Sr}^{90}/\text{Y}^{90}$ Beta Backscattering and Absorption combined process with different fixed absorbers over the sources.
a. 132 mg/cm² of Al over source 1.
b. 22 mg/cm² of Al over source 1.
c. 88 mg/cm² of Al over source 2.

was done for the three different thickness regions (Fig. 6).

In the present method, two $\text{Sr}^{90}/\text{Y}^{90}$ sources are used—one for the absorption and the other for the backscattering effect. Attempts were also made to utilize single source and to record simultaneously the absorption and backscattering effects from the measuring plate. But it has not been found feasible to maintain good geometry between the source and the G.M. tubes for the two processes simultaneously, viz. absorption and backscattering with only one source. The difficulty has been overcome with two separate sources each arranged to suit the best geometry appropriate to the individual process of absorption and backscattering.

Different beta emitters, such as S^{35} , Tl^{204} , $\text{Sr}^{90}/\text{Y}^{90}$, Ce^{144} , $\text{Ru}^{106}/\text{Rh}^{106}$, etc., can be used in gauges for measuring and controlling thicknesses of various ranges. Out of these sources, $\text{Sr}^{90}/\text{Y}^{90}$ has been chosen for the present method because of its relatively long half life (28 years) and large penetrating capacity (upto 2 mm of aluminium and 0.7 mm of steel). Moreover, the

principal beta radiation from $\text{Sr}^{90}/\text{Y}^{90}$ source being of high energy (0.54 Mev. for Sr^{90} and 2.25 Mev. for the daughter Y^{90}), reasonably thick window G.M. tubes may also be used. Lastly, it may also be mentioned that $\text{Sr}^{90}/\text{Y}^{90}$ source does not emit gamma rays and therefore shielding difficulties are relatively unimportant.

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[Original mss. received on 6.5.69]

Differential thermal analysis of some gypsum samples has been made with particular reference to their dehydration characteristics and their influence on the growth of insoluble anhydrite by heat treatment. From the area of the dehydration peak of gypsum, it has been established that the dehydration energy of these samples is not similar in each case and that the variation of this energy is due to the difference in the bond-strength of the OH groups in their gypsum lattice. Again, a gypsum sample having less stable OH groups in the lattice, yields, on dehydration, a soluble anhydrite which changes to its insoluble form at a much lower temperature than that obtained from a more stable gypsum structure. Further, a method has been developed for the estimation of dolomite in gypsum samples by DTA for their quality assessment.

Dehydration of Gypsum and Its Influence on the Transformation of Anhydrite

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Introduction

Gypsum is used extensively in fertilizer industry, e.g. for the manufacture of ammonium sulphate by the Merseburg process and sulphuric acid by gypsum-sulphuric acid process. The success of these processes has been found to depend on the nature of gypsum and its associated constituents. Roy¹ et al observed that to get a

suitable magma of good filterability from the Merseburg process, gypsum sample should have association with dolomite and be free from clay and other slimy materials. Similarly, the reactivity of anhydrites formed by dehydration of gypsum varies from sample to sample in the gypsum-sulphuric acid process².

It is known that anhydrite is formed on heating gypsum

above 250°C, its formation taking place through several stages of dehydration. On heating upto 150°C, gypsum changes first to hemihydrate which again dehydrates further at about 200°C forming a soluble anhydrite. At about 250°C or above, there is an exothermic reaction, which is presumably due to the formation of an insoluble anhydrite³⁻⁶. This temperature varies from sample to sample. Lulla³ et al observed that this transformation takes place at about 250°C in case of some Indian varieties. On the contrary, Atmaram⁴ et al reported a temperature of 340-410°C for a similar change. West⁵ et al and Gruver⁶ observed the same to occur at 360-370°C in the cases of some American and continental varieties of gypsum. Although the exact reason for this variation is not known till now, it seems that among others the stability of gypsum-lattice also influences this transformation. A study on the factors affecting the transformation characteristics of gypsum to anhydrites may be useful in routing the process variables involved in many reactions, which are utilized in fertilizer industry viz. gypsum-ammonium carbonate, gypsum-cement-sulphuric acid and gypsum-calcium sulphide-sulphur reduction as well as dehydration of synthesis gases and solvents by gypsum anhydrites.

In the present investigation, attempts have been made to study the transformation characteristics of anhydrites formed by dehydration of some gypsum samples with particular reference to the stability of their gypsum lattice.

Experimental

The following gypsum samples, all from Rajasthan, have been taken for the present investigations: (i) Dhirera, (ii) Kavas, (iii) Jamsar, (iv) Bikaner and (v) Utarlai varieties (Table 1). These were collected from

TABLE I—CHEMICAL ANALYSIS OF GYPSUM SAMPLES

Constituents	Dhirera	Kavas ¹	Jamsar ¹	Bikaner ⁴	Utarlai
Combined H ₂ O	16.50	14.36	19.49	19.55	17.70
CO ₂	4.30	4.27	1.28	1.04	0.63
SiO ₂	10.72	12.18	1.46	2.36	10.50
*R ₂ O ₃	0.82	2.11	2.60	0.21	0.66
CaO	29.95	30.08	31.56	32.19	29.71
MgO	1.26	1.08	0.10	0.18	0.51
SO ₃	36.43	35.74	45.77	44.43	39.55

*R₂O₃=Al₂O₃+Fe₂O₃

*of FCI Ltd.,

Sindri Unit* where they are utilized for the production of ammonium sulphate by Merseburg process. In order to remove the siliceous and other impurities, these samples were ground to 200 mesh (B.S.S.) size and washed several times with water. The washed samples were dried in air and finally over anhydrous silica gel in a desiccator for 12 hr. It has been found by thermogravimetric determination that all these washed samples consist of not less than 97 per cent CaSO₄·2H₂O.

The DTA instrument used for this work was a fully automatic Linseis model, having thermocouple of Pt/Pt-Rh (13 per cent) and sample-holders of thin platinum cylinders. The rate of heating was controlled at 10°C/min. by a programme controller. α -Al₂O₃ was used as a reference substance. Identical conditions were maintained in each case of DTA analysis. Exactly 1.5 g. of sample was used in each analysis. The DTA thermograms of the samples are shown in Fig. 1.

Estimation of Minor Constituents in Gypsum Samples: It has been observed from the DTA thermograms (Fig. 1) that peaks other than those of gypsum phase are due to dolomite only (at about 800 and 900°C). In order to determine the active mass (gypsum phase) in the samples, a quantitative idea of their associated constituents is necessary. Therefore, an estimation of their dolomite content has been made by DTA which can be used to estimate the same upto as low as 0.3 per cent which x-ray and other methods are unable to detect⁹. Again, the characteristic peak at 800°C is very sensitive and is unaffected by those experimental limitations which usually stand in the way of utilizing this technique for quantitative investigation¹⁰.

For the estimation of dolomite, the area of the peak appearing at about 800°C in the thermograms of each sample was measured after closing the two open ends (Fig. 1). The percentage of dolomite was determined from a previously-calibrated curve made from a mixture of a lime-stone and dolomite and utilized for the estimation of dolomite in lime-stone⁸. The validity of this method was checked by using a known mixture of a gypsum (Dhirera variety) and a dolomite (Table 2). The observed values have been found to be within 10 per cent agreement with the calculated values. The dolomite content of these samples are between 0.45 to 1.4 per cent (Table 3).

Dehydration Energy of the Gypsum Samples: The heat of decomposition of gypsum (dehydration energy) has been calculated from the DTA thermogram of the samples by using the following equation¹⁰.

$$\Delta H = \frac{gK_s}{m} \int_a^c ydt, \text{ where}$$

ΔH = heat of decomposition/g.,

m = mass of reactive component in the sample, g.,

k_s = thermal conductivity of the sample,

g = geometrical shape constant of the specimen holder,

$\int_a^c ydt$ = area of the peak enclosed between points of start (a) and end of reaction (c).

In the present case, the experimental parameters, like K_s and g , are similar in each sample as identical procedures had been followed and the same instrument utilized. The reactive mass 'm' was determined by deducting the amount of dolomite which was estimated in each case (Table 3). The area of the peak that appeared in the 150-190°C range was measured after closing the two open ends. The final peak area/g. of reactive mass was calculated (Table 4). Under the above experimental condition, the peak area is proportional to the heat of dehydration (ΔH) of gypsum. ΔH again is a measure of the energy of decomposition of gypsum. This decomposition is due to disruption of OH bond in the gypsum lattice. This peak area, when compared among themselves, is thus expected to reveal a variation in their bond energy if there be any such difference at all.

TABLE 2—DOLOMITE CONTENT IN PREPARED MIXTURE OF DHIRERA GYPSUM AND RISIKESH DOLOMITE

Sl. No.	Dolomite in the Mixture		
	Actual Quantity Added, %	Quantity Determined from Peak Area, %	Deviation, %
1.	0.90	0.82	-9.99
2.	2.00	1.80	-10.0
3.	3.60	3.50	- 2.8
4.	9.80	10.1	+3.06

TABLE 3—DOLOMITE IN GYPSUM SAMPLES

Sample	Dolomite, % by wt.
Dhirera	1.4
Kavas	1.05
Jamsar	0.45
Bikaner	0.60
Utarlai	0.54

TABLE 4—DEHYDRATION PEAK AREA AND EXOTHERMIC PEAK TEMPERATURE OF GYPSUM SAMPLES

Samples	Exothermic Peak Temperature, °C	Peak Area due to Dehydration/g. Active Mass, mm ²
Dhirera	250	1440
Kavas	280	1543
Jamsar	300	1874
Bikaner	580	2607
Utarlai	330	2049

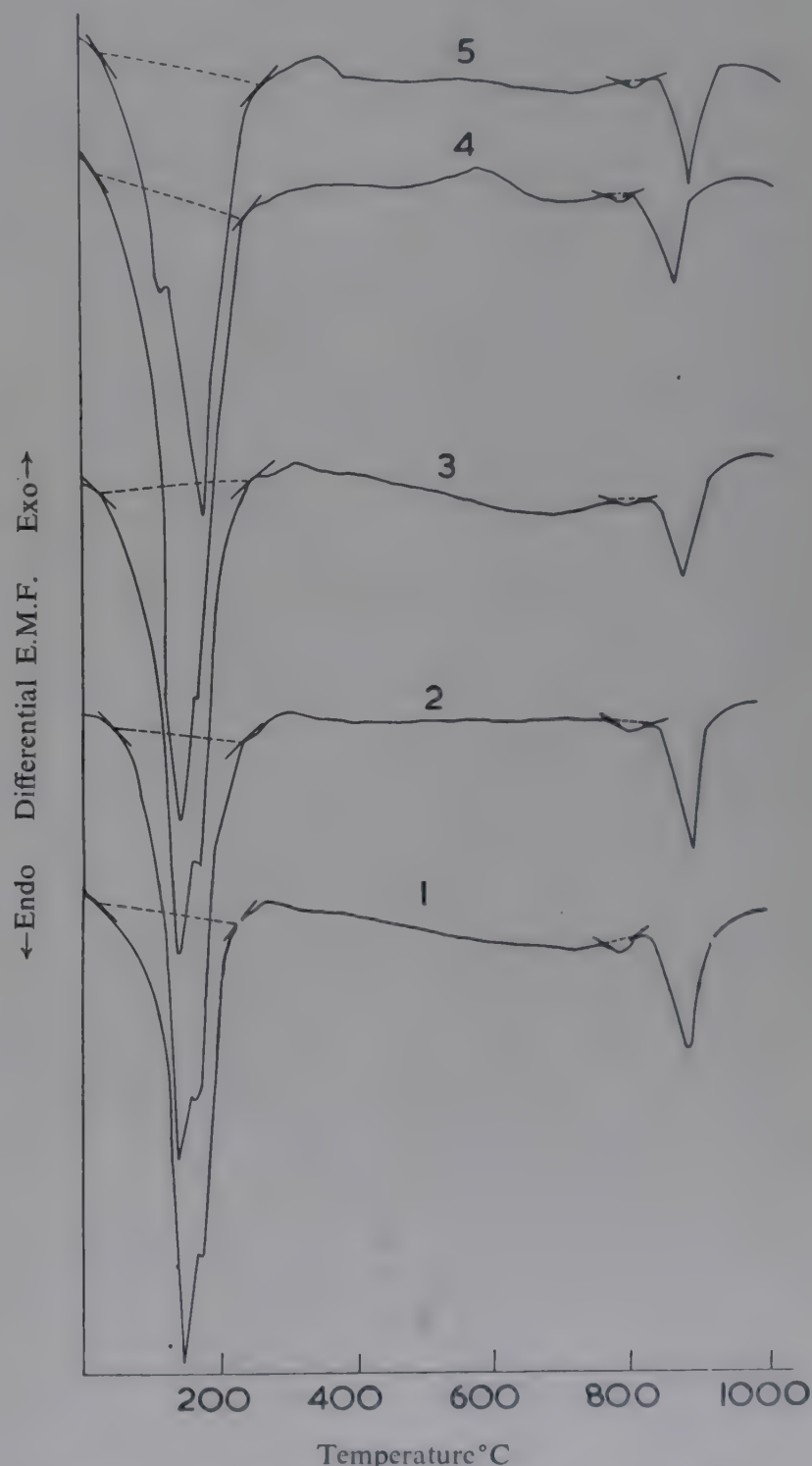


Fig. 1—DTA Thermograms of Gypsum Samples from Rajasthan

1. Dhirera, 2. Kavas, 3. Jamsar, 4. Bikaner, 5. Utarlai

Results and Discussion

It is evident from the DTA thermograms (Fig. 1) that the samples consist mainly of gypsum phase associated with a small amount of varying proportion of dolomite (Table 3). This dolomite content may, therefore, be useful in assessing their quality for the Merseburg process. Again, DTA thermograms of all samples show a double-natured endothermic peak in the region 150-190°C., which is known to be due to the dehydration of gypsum to its hemihydrate and then to soluble anhydrite (Fig. 1). Although this peak temperature is same in each case, yet the peak area is found to differ from sample to sample (Table 4). This peak area is a measure of dehydration energy of gypsum samples and this energy is very much related to the stability of the bonding of OH groups in the gypsum lattice. When these groups are more stable, more energy is necessary for their expulsion which causes an increase in the peak area value. It is, therefore, evident from the peak area values that the stability of OH groups in gypsum samples decreases in the following way: Bikaner > Utarlai > Jamsar > Kavas > Dhirera. There is also one exothermic peak in the thermograms of these samples (Fig. 1), which has been ascribed to the transformation of the soluble to an insoluble form of anhydrite. But its peak temperature varies for different samples. In the Dhirera variety, this temperature is lowest (i.e. 250°C), whereas in the case of Bikaner variety it is highest (i.e. 580°C). Again, in Bikaner and Utarlai varieties this peak is more prominent and appears at higher temperatures than in the cases of Dhirera, Kavas and Jamsar.

It is interesting to mention here that there is striking correlation between this transformation temperature and the area of the dehydration peak of gypsum samples. It has been observed that the transformation temperature increases with increasing peak area (Fig. 2). This may be explained on the basis of the observed stability of the OH groups in their gypsum lattice. It is likely that gypsum lattice having OH groups with less bonding energy changes on dehydration to a soluble anhydrite of a more unstable configuration, than that obtained from

a lattice of stronger bond energy. The more it is unstable, more is the tendency to change to an insoluble form at lower temperatures.

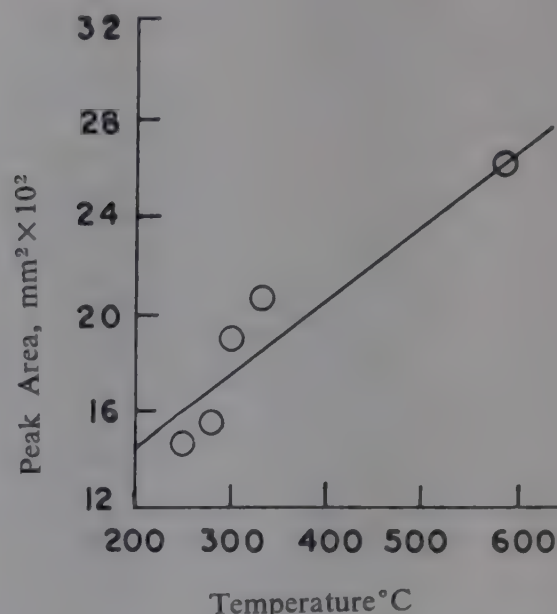


Fig. 2—Dehydration Peak Area Vs. Anhydrite Transformation Temperature of Gypsum Samples

Acknowledgement

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Differential thermal investigation on some Indian rock phosphates has been performed with particular reference to the role of their associated minerals and additives on the development of citrate-soluble compounds by heat treatment. When the rock phosphates are associated with calcite, clayey and iron minerals, there is some improvement in the citrate-solubility on heating upto 950°C but heating beyond this temperature does not increase it to a further extent. However, on mixing them with additives like mica, sodium sulphate and carbon and heating upto 1250°C, their citrate-solubility can be enhanced. Mica has particularly been found the most effective additive for iron-rich rock phosphates, whereas sodium sulphate and carbon for those associated with calcite and clayey minerals. It has been observed that iron compounds help fusion of the apatite in presence of mica and favour crystallization of a citrate-soluble compound, viz. α -tricalcium phosphate, from the melt. In presence of sodium sulphate and carbon, the apatite develops another citrate-soluble compound, like $10 \text{ CaO}, 2\text{Na}_2\text{O}, 3\text{P}_2\text{O}_5, \text{SO}_3, 2\text{SiO}_2$, which is favourably formed when the rock phosphates are associated with clayey and calcite minerals. Further, the constitution of apatite seems to influence the development of citrate-soluble compounds in the heat-treated mass in presence or absence of any of the additives.

Thermal Studies of Some Indian Rock Phosphates With or Without Additives

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The rock phosphate deposits of U.S.A., North Africa, Russia, France, Spain, Sweden and Pacific Islands are quite suitable for making phosphatic fertilizers by the conventional process¹⁻⁵. But in India the available deposits are of a low grade and therefore their conventional processing for fertilizers is uneconomical. However some attempts have been made to enrich the low and medium grade calcareous phosphorites by using thermal methods, such as roasting at 900-950°C and then sudden cooling of the products^{6,7}. There had been attempts to prepare citrate-soluble phosphatic fertilizers from low grade rock phosphates by thermal treatment using various additives like sodium sulphate and carbon, feldspar, etc.^{8,9}.

Low grade rock phosphates are usually associated with various constituents other than apatites. The interaction of the latter with these constituents as well as with additives at elevated temperature is likely to influence the quality of the heat-treated phosphates. To achieve success on this thermal process, a knowledge of their mineralogical composition as well as thermal behaviour with or without additives is of primary importance. But very little is known on the physico-chemical properties of Indian rock phosphates, particularly on the nature of physical and chemical changes as effected by thermal

treatment. The present work has, therefore, been taken up to study this mineralogical composition as well as thermal behaviour using some samples of different origin with or without additives.

Experimental

The rock phosphate samples taken for this investigation are designated as Jaisalmer, Singbhum, Vizag unwashed and washed. One imported rock sample (Makatea variety) of a very good quality was also studied. Their chemical composition (Table 1) indicates that the P_2O_5 content in them varies from 25.1 to 37.8 per cent.

Differential Thermal Analysis: DTA of the samples was carried out in a fully automatic Linseis instrument in the range of 30-1250°C, using Pt/Pt-Rh (13 per cent) thermocouples and thin cylindrical sample holders of platinum. This instrument was designed to run three different samples at a time. The rate of heating was controlled at about 10°C/min. by a programme controller. α -alumina was used as a reference substance. The identification of phases was done by noting different peak temperatures of exo- and endothermic peaks.

DTA of the samples with additives, like (i) mica (4:1) and (ii) sodium sulphate and carbon (7:2:1) was also performed in the above manner. The thermo-

TABLE 1—CHEMICAL COMPOSITION OF DIFFERENT ROCK PHOSPHATES, % BY WT.

Constituents	Jaisalmer Apatite	Singbhum Apatite	Vizag		Makatea (Pacific Coast)
			Unwashed	Washed	
P ₂ O ₅	27.35	25.10	25.10	37.50	37.80
SiO ₂	4.92	14.46	20.23	2.50	00.10
CaO	45.50	33.68	35.20	49.50	51.65
MgO	0.08	2.81	—	—	—
Fe ₂ O ₃	1.69	14.93	2.50	1.50	1.14
Al ₂ O ₃	—	5.14	6.58	—	—
Cl ₂	—	1.37	0.48	0.55	—
F ₂	4.35	0.84	2.85	3.47	2.79
CO ₂	11.63	—	1.10	1.20	1.30
SO ₂	1.15	—	—	—	0.17
Na ₂ O	0.95	—	—	—	—
K ₂ O	—	—	—	—	—
Undetermined	2.38	1.67	5.99	3.78	5.05

grams are shown in the Figs. 1,2 and 3, and the peak temperatures in Table 2.

Thermal Treatment of Rock Phosphates and Determination of P₂O₅: About 2 g. of each of these samples powdered to -200 mesh (B.S.S.) were heated to 1250°C separately either as it is or mixed with the desired additives like (1) mica dust* (in the ratio 4:1) and (2) sodium sulphate and carbon (7:2:1) in a crucible of magnesite brick for 1 hr. The samples were also heated without any additives to 950°C and 1250°C for same period. P₂O₅

content of these samples before and after heat treatment were determined by the method of Kumar¹⁰ et al. Their citrate-soluble P₂O₅ was also determined by this method after treating the samples in neutral ammonium citrate solution in accordance with the A.O.A.C. procedure¹⁴.

In this method the rock phosphate (c 0.1—0.2g.) was digested in a platinum-crucible with a mixture of perchloric hydrofluoric and boric acids. The digested mass was dissolved in a mixture of water and nitric acid, the phosphate was precipitated by adding an excess of

TABLE 2—DTA DATA OF ROCK PHOSPHATE SAMPLES WITH & WITHOUT ADDITIVES
Peak Temperatures (°C) & Intensities

Sample	Without Additives		Mixed with Mica Dust (4:1)		Mixed with Na ₂ SO ₄ & C (7:2:1)	
	Endothermic	Exothermic	Endothermic	Exothermic	Endothermic	Exothermic
Jaisalmer	120 m 860 s		120 w 1100 *		250 w, 850 s, 870 s, 920 *	350-400 m bulge
Singbhum	130 w 350 w 550 w	960 w	180 w 520 w 900 *	100 w	230 w, 750 *	350 w bulge
Vizag unwashed	170 s 850 w 1220 sm	960 w	1210 w 1220 *	840 w	120 w, 250 w 840 m, 900 *	350-380 m bulge
Vizag washed	170 m 860 w 1200 w	960 w	110 w 1210 w 1100 *	840 w	230 w, 750 s 850 *	350-380 w bulge
Makatea	120 w 750 w 860 w 1180 w bulge	720 w	180 w 1180 w 1250 *		250 w, 800 s, 1040 *	350-380 w bulge

s—strong, m—medium, w—weak.

* Sintering Temperature

*SiO₂=36.42, Fe₂O₃=8.91, Al₂O₃=23.58, CaO=2.70, MgO=17.11, Alkali=3.10, L.O.I.=6.06 and Moisture=2.06 per cent

standard zirconium nitrate solution and the excess zirconium solution was back-titrated with a standard solution of E.D.T.A. using xylenol orange as an indicator. The results are given in the Table 3.

Results and Discussion

The associated minerals, identified from the DTA thermograms, are calcite (endothermic peak at 850°-860°C) in all samples except in the Singbhum variety, illitic clay (endothermic peaks at 170°, 550° and one exothermic peak at 960°C) in Vizag (both washed and unwashed) and Singbhum varieties and iron mineral like goethite (endothermic peak at 350°C) in Singbhum variety. Fe₂O₃ content of the last sample is as high as 14.93 per cent (Table 1). The proportion of these constituents varies from sample to sample as is evident from the intensity of their peaks (Fig. 1, Table 2). The amount of calcite is much higher in the Jaisalmer than in the Makatea and Vizag varieties and that of illitic clay is much less in the washed than the unwashed Vizag variety.

By heating alone upto 1250°C, there is a little improvement of the citrate-solubility of the rock phosphate samples. But it is interesting to mention here that with the Makatea variety the citrate-solubility falls considerably when heated beyond 950°C (Table 3), and unlike others, it shows an endothermic peak at 750°C (Table 2, Fig. 1), which is known to be due to the presence of carbonatoapatite; the latter changes to oxy-apatite beyond this temperature¹¹. The decrease in citrate-solubility may be due to the transformation of this apatite to oxy-form, which is insoluble in citrate solution.

When the rock phosphate samples are mixed with mica and heated to 1250°C, the citrate-solubility developed

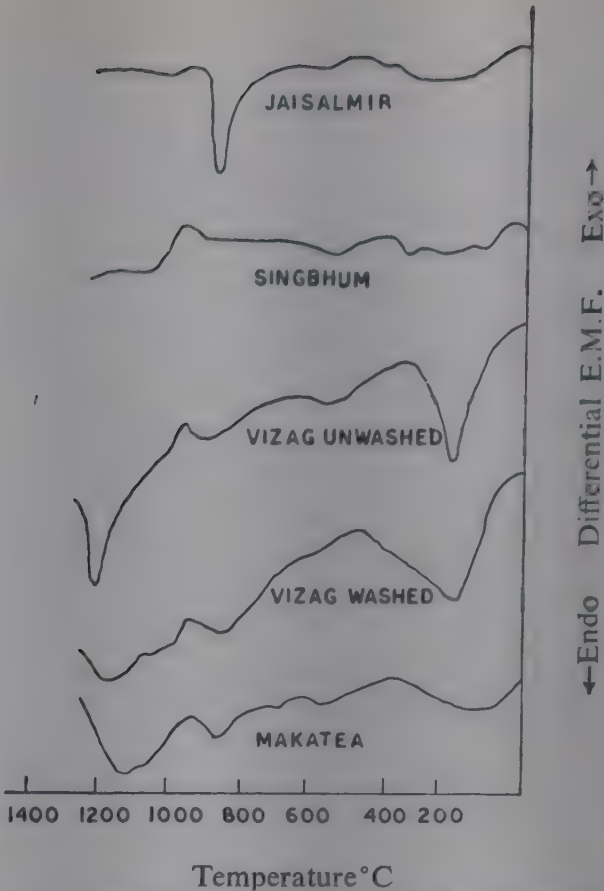


Fig. 1—DTA Thermograms of Rock Phosphates

is more than those heated without any additive (Table 3), but with the Singbhum variety, this improvement is more prominent than in the others. From the DTA investigation (Fig. 2, Table 2), it is evident that the fusion of its mixture with mica starts as low at 900°C. No such fusion occurs even at 1100°C in other samples. The low fusion temperature of this mixture is evidently due to the presence of an appreciable quantity of iron mineral. Iron compounds are known to be good fluxing agents in CaO-SiO₂-P₂O₅ system. Preliminary x-ray diffraction study reveals that α-tricalcium phosphate, which is citrate-soluble, is formed as a result of this fusion.

TABLE 3—TOTAL AND CITRATE-SOLUBLE P₂O₅ OF ROCK PHOSPHATE SAMPLES HEATED WITH OR WITHOUT ADDITIVES AT DIFFERENT TEMPERATURES, %

Samples	P ₂ O ₅ Content (as such)		P ₂ O ₅ Content (Heated to 950°C)		P ₂ O ₅ Content (Heated to 1250°C)		Sample+Mica (4:1) P ₂ O ₅ Content (Heated to 1250°C)		Sample+Na ₂ SO ₄ +C (7:2:1) P ₂ O ₅ Content (Heated to 1250°C)	
	Total	Citrate-Soluble*	Total	Citrate-Soluble*	Total	Citrate-Soluble*	Total	Citrate-Soluble*	Total	Citrate-Soluble*
Jaisalmer	27.5	12.0	30.4	13.4	30.4	10.5	24.1	19.0	26.4	89.0
Singbhum	25.1	1.5	25.2	3.6	25.1	5.1	21.5	46.5	24.4	73.1
Vizag unwashed	25.1	2.3	25.1	6.3	25.1	6.3	25.7	21.7	22.0	81.8
Vizag washed	37.5	1.8	37.79	4.7	37.3	6.1	32.1	20.8	33.2	50.30
Makatea	37.8	11.6	37.06	13.1	35.3	0.0	29.4	17.2	29.8	19.7

*Solubility percentage calculated on the basis of the respective total P₂O₅ content of the samples.

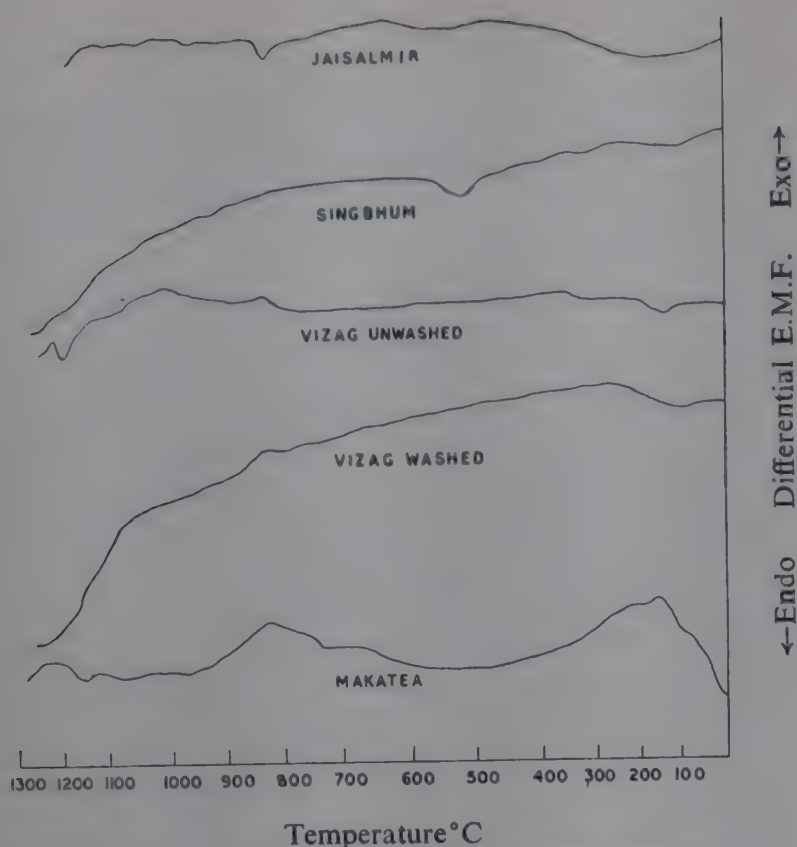


Fig. 2—DTA Thermograms of Rock Phosphates Mixed with Mica Dust (4:1)

When sodium sulphate and carbon are used as additives and heated to the same temperature as in the case of mica admixture, the citrate-solubility is still more enhanced except in the Makatea variety, which is virtually unaffected (Table 3). The nature of interaction of these additives with rock phosphates can be visualized from their DTA thermograms (Fig. 3). The nature of their thermograms is, however, similar to each other; each showing peaks at 250-280°, 350-400° and 750-850°C, the first two peaks being due to phase transition of sodium sulphate¹³ and oxidation of carbon respectively. The last peak, which is double-natured and is evidently due to melting of sodium sulphate and possibly interaction of the sulphate melt with rock phosphate, is followed by a strong downward trend occurring around 750-1040°C (Table 2). This downward trend of the thermograms indicates sintering of the mass. In case of Makatea variety the sintering temperature is highest (Table 2). Therefore, the state of sintering of this mass at 1250°C is lowest of all, which indicates that there is a less chance of crystallization of any compound from its melt formed as a result of sintering.

One of the reasons for its low sintering may be due to its small admixture with calcite which causes a lowering of the sintering temperature and helps the formation of a citrate-soluble compound⁸ like $10\text{CaO} \cdot 2\text{Na}_2\text{O} \cdot 3\text{P}_2\text{O}_5 \cdot \text{SO}_3 \cdot 2\text{SiO}_2$. It is also quite possible that the oxyapatite formed from carbonato-apatite constituent of Makatea variety on heating does not react so easily with

the sodium sulphate and carbon; besides, the chemical analysis (Table 1) shows that it contains very little of silica. As silica is necessary for the formation of the citrate-soluble compounds, like $10\text{CaO} \cdot 2\text{Na}_2\text{O} \cdot 3\text{P}_2\text{O}_5 \cdot \text{SO}_3 \cdot 2\text{SiO}_2$, the latter has not formed because of low silica content of this sample.

It is interesting to mention here that the sintering temperature of the Singbhum variety is lowest, in spite of which its citrate-solubility is somewhat less than those of Jaisalmir and Vizag (unwashed) samples (Table 3). Low sintering temperature is possible because of its high Fe_2O_3 content (Table 1) and possibly of the formation of a ferruginous compound, which is less soluble in citrate-solution in the sintered mass.

Again, it may be incidentally mentioned here that Vizag and Makatea varieties show a high temperature peak in the 1180°-1220°C. The presence of this peak indicates that the apatite constituent of these rocks differs from the fluoro-apatite, which does not have any peak in its thermal diagram. This peak is, however, known to appear in case of lazulite—a carbonato-apatite group of minerals¹². This shows that the lazulite character of the rock phosphate samples is still retained even at that temperature and is unaffected by the sodium sulphate

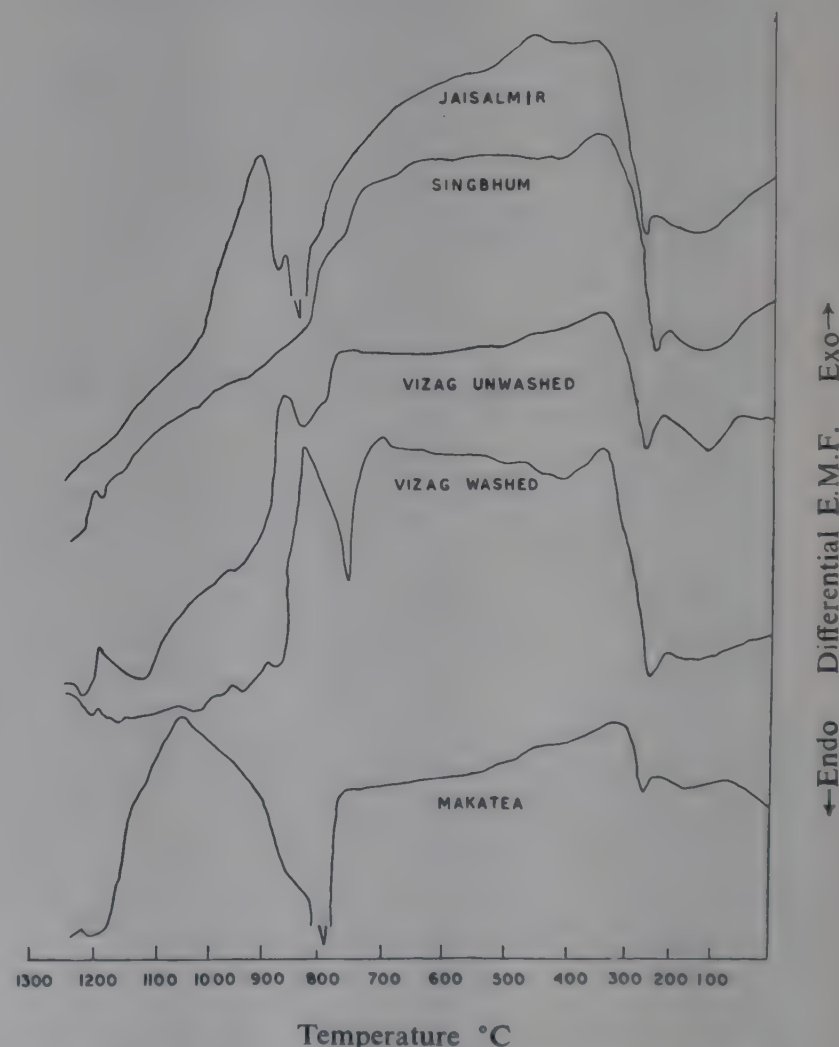


Fig. 3—DTA Thermograms of Rock Phosphates Mixed with Sodium Sulphate and Carbon (7:2:1)

and carbon. But in case of Vizag unwashed variety, there is a marked increase in the citrate-solubility, although the same peak is present in its DTA thermogram. This shows that the siliceous materials (illitic clay) favour interaction of this apatite with sodium sulphate and carbon at the elevated temperatures.

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Thanks are due to Dr. B. K. Banerjee, Addl. Superintendent (PRW), P & D Division, for his active encouragement. Thanks are also due to Sri S. Mukherjee for x-ray diffraction analysis of one sample.

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Biuret has been estimated indirectly by atomic absorption spectrophotometer (AAS), by complexing it with copper in alkaline medium and utilizing the linear relationship between the copper absorbance and biuret concentration. It was observed that freshly precipitated suspension of copper hydroxide, prepared by mixing copper sulphate and potassium hydroxide, is unsuitable. However, the above suspension, when kept for 5 to 20 hours after preparation, gave good results. This method is sensitive and accurate and can be used for determination of low concentrations of biuret in urea.

Estimation of Low Content of Biuret in Urea by Atomic Absorption Spectrophotometry

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Introduction

There are several photometric methods for estimation¹⁻⁵ of biuret in industrial grade urea based on its reaction with copper in alkaline medium. In this laboratory Sanyal and Pal⁵ estimated biuret photometrically by complexing it with cobaltic salt. However, the sensitivity of these photometric methods is inadequate for biuret concentration below 0.5 per cent in the samples.

Geurts et al⁶ have developed an excellent method for estimation of biuret by separating the copper-biuret anion from the complex by an anion-exchange resin. The adsorbed anion is eluted with 100 ml. of 2M potassium nitrate and 100 ml. of 0.2M nitric acid solutions. The elute was titrated for bound-copper with EDTA and the corresponding biuret content was calculated with the help of copper to biuret stoichiometric ratio

in the complex. The advantage of this method is that biuret can be concentrated by taking more urea sample, which is not adsorbed by the exchanger. The blank copper which was a source of trouble for estimating the bound-copper in the complex also percolates through the resin.

Biuret reaction has also been used for the estimation of proteins^{7,8} and amino nitrogen^{8,9}. Beauchene et al⁹ have estimated nitrogen content in amino acids and hydrolysed proteins by complexing them with copper phosphates at pH 9.2 and then estimated the bound-copper with flame photometer. Estimation of biuret in the present investigation was tried on similar lines. Copper complex was preferred over nickel and cobalt complexes because copper determination by atomic absorption spectrophotometric method is easier and more accurate. For preparing the complex, the usual method¹ was used.

It has been observed that by varying the parameters, such as, pH, legend to copper ratio, reaction time and centrifuging and shaking time, the bound as well as blank copper vary. Though the bound-copper absorbance increases with the biuret content, no rigid relationship exists between them. It was also observed that with time the bluish colour of the copper hydroxide changes to greyish black. To stabilize the above condition, different concentrations of potassium hydroxide and copper sulphate solutions were mixed and kept for 5 to 6 hr. to allow them to turn completely to a greyish black fine precipitate. This copper hydroxide suspension was used for complexing biuret with copper. By using the above suspension after 5 to 6 hr. of its preparation and upto 20 hr. a linear relationship between copper absorbance and biuret content was obtained, though an exact stoichiometric ratio between copper and biuret did not exist. This relationship was utilized for the estimation of biuret in urea. With small changes in the keeping time of copper hydroxide suspension after 5 hr. the absorbance did not change significantly. The mixture which was finally selected for the present work was having 3 per cent potassium hydroxide and 1.6 per cent copper sulphate pentahydroxide. The copper to biuret ratio, just after 5 hr. of keeping the mixture, was very near to the stoichiometric ratio.

The standard addition technique was used for biuret in urea by the present method. The addition curve for one unknown sample was used as a calibration curve for other unknown samples. The preparation of all the samples was done simultaneously, and urea content in all of them was kept same. The effect of urea on the absorbance of copper was also studied, and it was

found that upto 2 per cent of urea content, there was practically no change in the absorbance values (Fig. 1).

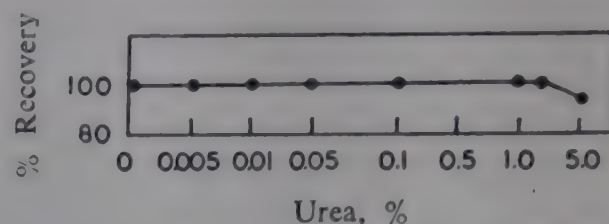


Fig. 1—Recovery of 5 ppm of Copper in Presence of Urea

Experimental

Sample Preparation: A copper hydroxide suspension was made in distilled water by mixing 80 ml. of copper sulphate pentahydrate (20 per cent) solution and 100 ml. of potassium hydroxide (30 per cent) solution in 1 litre pyrex volumetric flask and thoroughly shaken. It was kept at room temperature for 5 to 6 hr. when the precipitate became greyish black and fine.

20 ml. each of the copper hydroxide suspension was taken in 14 centrifuge tubes each of 50 ml. capacity. In one tube 5 ml. distilled water was added and this solution was used as a blank. In other three tubes 5 ml. of 50, 100 and 150 ppm biuret solutions were added respectively. For finding out the reproducibility of the method, 5 ml. of 100 ppm of biuret solution was added in the above suspension in other 10 tubes.

For the addition method, 20 ml. of the suspension was taken in eight tubes and the blank was prepared in one tube as above. In the other three tubes, 2.5 ml. of 1 per cent urea sample A was added. In the first tube, 2.5 ml. of water and in two other tubes 2.5 ml. of 50 and 100 ppm. biuret solution was added respectively. In the other four tubes 5 ml. of 0.5 per cent of unknown urea samples were added. A separate set of four addition samples were made for estimation of low quantity of biuret in analytical grade urea (AR) sample. These addition samples were made similar to the above sample A, by suitably adjusting the urea content.

All the standards and samples were kept for 5 to 10 min. and then centrifuged for 4 min. at 3000 rpm. The clear aliquots were cautiously aspirated directly from the tube into the flame.

Procedure

A Perkin-Elmer model 303 atomic absorption spectrophotometer, equipped with premix acetylene burner-head, was used. The copper hollow cathode lamp was also of Perkin-Elmer make, and the analytical condi-

tions were same as suggested by them¹⁰. The blank was aspirated and zero was adjusted by the zero-adjustment knob. The sample absorption was directly noted for bound-copper in all the samples. The standard addition curve for sample A is shown in Fig. 2. The same curve was used to determine the biuret content in other unknown samples (Table 1). Biuret in the AR urea sample was estimated separately.

TABLE 1—BIURET CONTENT IN UREA

Sl. No.	Urea samples	Biuret by AAS Method %	Biuret by Photometric Method, %	Deviation
1.	A	0.91	0.92	-0.01
2.	B	1.58	1.51	+0.07
3.	C	1.00	1.10	-0.10
4.	D	1.01	1.01	0.00
5.	E	1.92	1.91	+0.01
6.	AR	0.14	—	—

Results & Discussion

The standard deviation of the method for the determination of 20 ppm biuret in solution was found to be ± 1.2 per cent. This method is very sensitive and accurate and biuret upto 50 ppm can be estimated accurately in urea samples. It is superior to the photometric methods

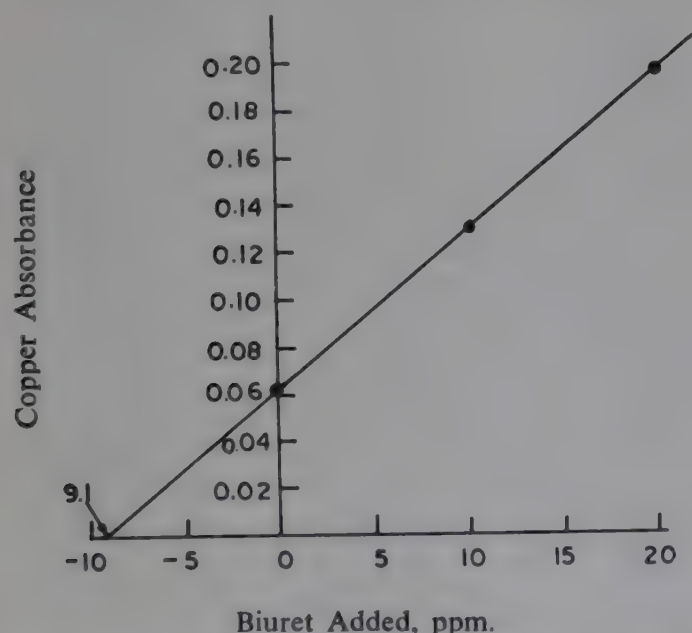


Fig. 2—Standard Addition Curve for Sample A and Used as Calibration Curve for Samples B to E

and is also quicker than the Geurts' method⁶, as the ion-exchange step is eliminated. As the determination of copper by atomic absorption does not suffer any interference in the presence of other ions, this method can also be utilized for biuret estimation in mixed fertilizers. Though the stoichiometric ratio of copper to biuret was not obtained, it did not prove to be a handicap as the copper absorbance and biuret content relationship was found to be linear. The non-stoichiometric ratio of copper to biuret may be either due to the pH or excess of ligand to copper ratio¹¹ or vice versa. It may also be due to the adsorption of the complex by copper hydroxide suspension.

The only drawback in the present method is that the experiment can be started only after keeping the copper hydroxide suspension for about 5 hr. Since the copper to biuret ratio is changing with time, with every set of samples new standards will have to be prepared, in case there is much time difference between the different sets of analysis. Lower limit can be further achieved by using the high solid content burner, thereby aspirating more concentrated solution in the flame.

Acknowledgement

Thanks are due to Dr. A. K. Gupta, Chief Chemist, FCI Ltd., Sindri Unit, for supplying the analysed urea samples

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Mineralogical investigation on some micaceous deposits from *Kasipatnam* area has been made by differential thermal and x-ray diffraction analysis. These deposits are found to consist of mainly biotite with small proportions of chlorite and vermiculite. In the biotite lattice, there are possibly some interstratifications in the layers. and the vermiculite and chlorite are found to be of highly ferruginous type, having a large number of Fe^{2+} ions in their lattice. This vermiculite shows one exothermic peak at 310-380°C immediately after the initial dehydration in the thermogram. This peak is presumably due to oxidation of Fe^{2+} ions present in the lattice. Further, it is probable that those minerals are formed as a result of alteration of trioctahedral biotite mica and this alternation is not uniform in these deposits.

Mineralogical Study of Some Indian Micaceous Deposits from Kasipatnam Area (Andhra Pradesh)

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In India, the deposits of mica are very large and in many of them various alteration products, such as vermiculite, are present in varying proportions. One of such deposits has been found in *Kasipatnam* area (Andhra Pradesh), where vermiculite-type minerals associated with biotite mica have been reported¹⁻³. Since vermiculites are formed by the alternation of mica, pyroxene, chlorite or other similar minerals, they are very often associated with them.

Although the occurrence of vermiculites has been reported frequently in recent times, their x-ray diffraction data, except those for basal and 060 reflections, are very limited. The basal reflection of vermiculite is usually very strong and subsequent reflections are quite weak. If the mineral is trioctahedral, the 060 reflection is in the region 1.53 Å and for di-octahedral at about 1.50 Å. When chlorites are associated with vermiculites, their identification is rather difficult. They have similar basal reflection as that of vermiculites. Although in case of chlorites this reflection is less intense than that of vermiculites, yet when the first few basal orders of reflection are not clearly seen, their identification may be difficult by x-ray study alone. Again, ferruginous chlorites create additional difficulties in identifying them in presence of vermiculites. Their 001, 003 and 005 reflections are relatively weaker than those of

magnesium chlorites. Besides, some ferruginous chlorites have been reported, which when heated show remarkably uniform exfoliation, similar to that of vermiculites⁴. Brindley and Gillery⁵ also found that in case of iron-rich chlorites, the basal intensity could not be reconciled with the usual chlorite structure. If x-ray data are utilized along with differential thermal analysis results, their identification becomes relatively easier. Vermiculites can be identified by DTA⁶ as they usually show well-defined endothermic peaks in the region 140-225 and 240-325°C and at about 900°C. in their thermograms. The last peak is sometimes double-natured. Magnesium chlorites, on the other hand, show a prominent endothermic peak at 600-700°C and one at about 800°C. The latter peak is immediately followed by one exothermic peak at about 850°C. But the last endo and exothermic peaks may be absent in the thermogram of ferruginous chlorites. Instead, the main peak is immediately followed by an exothermic bulge. Further, with iron-rich chlorites, this peak appears at a lower temperature than that of magnesium chlorite⁶. The appearance of the bulge is due to oxidation of the ferrous ions which are usually present in the structure of ferruginous chlorites⁷. So, a combined effort by x-ray and DTA investigations of such deposits consisting of various alteration products of mica may be useful for their mineralogical assessments.

Till now, there is no information available regarding the structural characteristics and mineralogical peculiarities of the Indian ferruginous chlorites. Nor have any deposits of vermiculites, occurring in association with ferruginous chlorites been reported so far. Considering the above, an attempt has been made in this investigation to study the mineralogical compositions of some micaceous deposits from *Kasipatnam* area consisting of various alteration products of mica.

Geology

Kasipatnam, from where the mica samples have been collected, comprises an area of densely wooded hills in the Eastern Ghats, and falls in the Survey of India toposheets Nos. 65 N/3 and 65 N/4, 41 miles N.N.W of Visakhapatnam (A.P.). It forms, as a whole, the most highly metamorphosed portion of the Indian Archaean and is essentially characterized by rocks of unusual composition which includes some graphitic garnet sillimanite gneiss known as 'Khondalite', a variable series of calc-gneisses, some garnet-biotite gneisses, diopside-magnetite garnet gneiss, hypersthene-biotite gneiss, granite gneiss, pyroxene granulites and occasional hypersthene-gneiss. The more or less profuse development of garnet in the rocks shows a high degree of metamorphism possessed both by sedimentary and igneous members of the *Archaean* in this region. The anti-stress minerals, like sillimanite, pyroxene and graphite, are also very characteristic in this area, and at places many of the above-mentioned rocks show signs of severe stress also.

The country rock is traversed by a large number of pegmatites veins along the joints developed in the rocks. The thicker veins, which mainly traverse the calc and diopside gneiss, are highly mineralized and are confined only to the N. 50°W to S 50°E joints out of the three sets of prominent joints in the area. These thick veins occurring in this calc and diopsidic rocks contain the above micaceous minerals along with apatite, magnetite, zircon, diopside, quartz and feldspars, of which the hyalophane is an important one and rarely columbite-tantalite, copper, tremolite-actinolite, tourmaline and epidote. These minerals, which are golden brown to dark brown in colour, were reported earlier¹⁻³ as vermiculite and there are light greenish tinges also in some of the spots on them. These are also found to exfoliate and their colour usually changes to bronze yellow on heating. The thickness of the veins also varies from a meter to over 170m. in length and a few centimetres to a few metres in thickness. They occur mainly at the contact of country rock with the thick veins, and in some veins 3 to 4 zones are developed along with apatite and magnetite at regular

intervals. Generally, these micaceous minerals occur as coarse flakes upto 30 mm. thickness but books measuring much bigger than this are also present. Their physical appearance shows a hexagonal form with zoning in the centre in some cases.

Experimental

The samples taken for this investigation are designated as B-9, J, Pedda-Konda and SR-5C, in accordance with the vein names. Their chemical composition is given in Table 1.

TABLE 1—CHEMICAL COMPOSITION OF MICACEOUS MINERALS COLLECTED FROM DIFFERENT VEINS, % BY WT.

Constituents	J	SR-5C	Pedda-konda	B-9
SiO ₂	36.02	39.14	40.86	40.90
Al ₂ O ₃	19.46	18.97	20.64	19.96
TiO ₂	0.37	0.38	0.33	0.32
Fe ₂ O ₃	6.57	6.25	5.98	2.01
FeO	1.98	2.00	1.91	12.81
CaO	0.60	0.89	0.17	0.21
MgO	7.22	8.00	8.50	7.05
Na ₂ O	0.26	0.24	0.24	0.35
K ₂ O	7.62	7.88	8.83	8.76
H ₂ O ⁺ } H ₂ O ⁻ }	16.20	12.80	8.90	5.44
Ignition loss	3.50	3.50	3.38	2.32

X-ray Analysis: X-ray diffraction patterns of the samples were taken by a Guinier focussing camera with monochromatic CuK α radiation in a Philips PW 1010 x-ray unit at 40 KV and 20 mA. The time of exposure was 6 hr. The diffraction data are given in Table 2.

Differential Thermal Analysis: DTA of these samples was carried out in a fully automatic Linseis instrument in the range 30-1000°C. The thermocouples were Pt/Pt-Rh (13 per cent) and a nickel block was used as the sample holder. This instrument was designed to run three different samples at a time. α -Alumina was used as a reference sample. The rate of heating was controlled at about 10°C/min. The identification of phases was done by noting the different exo- and endothermic peak temperature. The thermograms are shown in Fig. 1, and the peak temperatures in Table 3.

Results and Discussion

It is evident from the x-ray diffraction data (Table 2) that among the samples only J and SR-5C show a very

TABLE 2—X-RAY DATA OF MICACEOUS DEPOSITS

Samples										Standard			
SR-5C					Pedda Konda					Biotite ^a			
B-9					Vermiculite ^a					Chlorite ^a			
dÅ	I	dÅ	I	dÅ	I	dÅ	I	dÅ	I	hkl	dÅ	I	hkl
14.0B	vw	14.0B	vw	—	—	—	—	—	—	—	14.2	3	001
11.0} B	m	11.0} B	m	11.0} B	m	10.1	vs	—	—	—	—	—	—
10.2}		10.2}		10.2}		—	—	—	—	—	—	—	—
4.65	vw	4.65	vw	4.65	vw	—	—	4.60	s	021; 111	4.68	2	003 020
4.58	vw	4.58	vw	4.58	vw	4.58	w	—	—	—	—	—	—
3.98	vw	3.98	vw	3.98	vw	—	—	—	—	—	—	—	—
3.60	vw	3.60	vw	3.60	vw	—	—	3.602	m	008	—	—	—
3.53	vw	3.53	vw	3.53	vw	—	—	—	—	—	3.55	8	004
3.40	vw	3.40	vw	3.40	vw	—	—	—	—	—	—	—	—
3.36	m	3.36	m	3.36	m	3.36	vs	—	—	—	—	—	—
3.14	vw	3.14	vw	3.14	vw	3.15	vw	—	—	—	—	—	—
2.92	vw	2.92	vw	2.92	vw	2.91	vw	2.873	m	0.0.10	2.85	—	005
2.64	vw	2.64	vw	2.64	vw	—	—	2.657	mw	130; 200; 202	2.68	3	200
2.62	s	2.62	s	2.62	s	2.65	s	2.602	ms	132; 204	—	—	—
2.50	vw	2.50	vw	2.50	vw	2.51	w	—	—	—	2.52	5	202
2.42B	m	2.42B	m	2.42B	m	2.45	s	—	—	—	2.43	—	025
2.30	vw	2.30	vw	2.30	vw	2.28	vw	2.277	vw	136; 208	—	—	—
2.17	w	2.17	w	2.17	w	2.183	s	—	—	—	—	—	—
1.99	vw	1.99	vw	1.99	vw	2.002	s	2.016	w	208	—	—	—
1.74	vw	1.74	vw	1.74	vw	1.752	vw	1.744	mw	2.0.14	—	—	—
1.67	vw	1.67	vw	1.67	vw	1.672	s	1.673	mw	1.3.14; 2.0.12	—	—	—
1.54	s	1.54	s	1.54	s	1.551	—	1.537	—	060; 1.3.16; 2.0.14;	1.557	5	060
1.51	vw	1.51	vw	1.51	vw	1.527	—	1.506	vw	330; 332; 334	—	—	—
1.32	vw	1.32	vw	1.32	vw	—	—	1.319	mw	332; 336	1.521	3	06
						—	—	—	—	2.0.20; 400; 406	1.323	1	402

s = strong, m = medium, w = weak, vw = very weak, vs = very very weak, B = Broad, I = relative intensity.
 Monochromatic CuK α radiation used.

Bold figures stand for figures with bars.

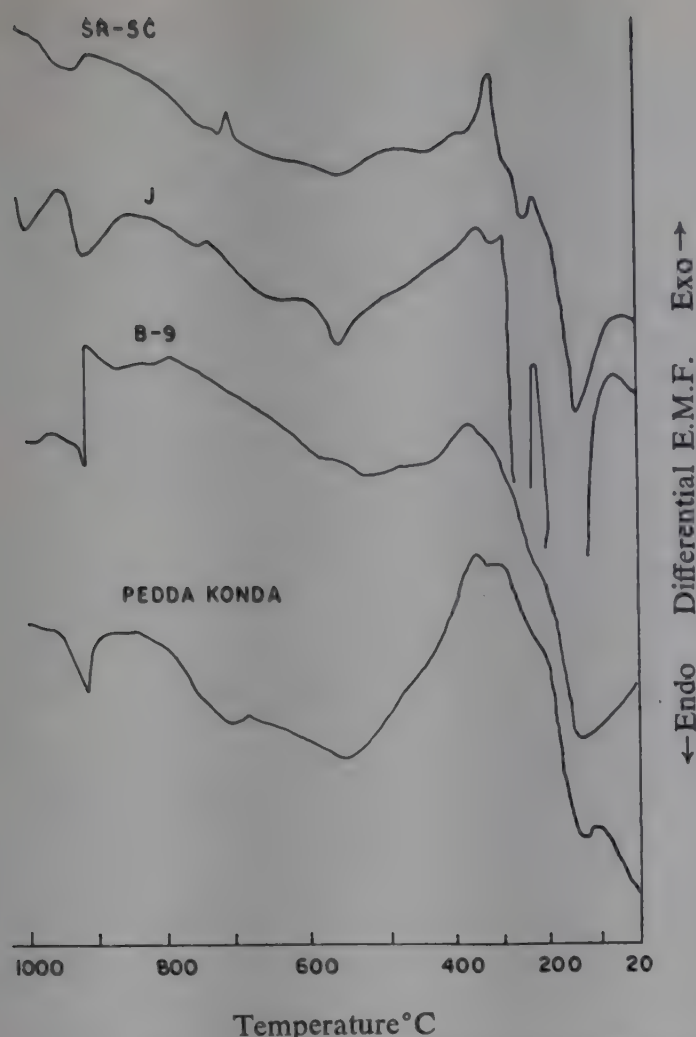


Fig. 1—DTA Thermograms of Micaceous Deposits from Kasipatnam Area

weak reflection at 14.00 Å. Except these, the diffraction data of all the samples are similar to each other. From these, biotite has been identified clearly as most of the reflections correspond to those of standard trioctahedral biotite mica. This has also been confirmed from chemical analysis (Table 1), which shows that these samples contain a very high proportion of K_2O (7.62-8.83 per cent). As K_2O content of biotite is known to be as high

TABLE 3—DIFFERENTIAL THERMAL ANALYSIS DATA OF THE MICACEOUS MINERALS
[Peak Temperatures in °C and Intensities]

Sample	Endothermic	Exothermic
SR-5C	140, m; 240, w; 560, w; 920, w;	310, m; 690, w;
J	150, s; 250, s; 560, m; 910, m; 990, m;	330, w; 730, w;
B-9	140, m; 240, wB; 540, wB; 920, m;	380, w; 790, w;
Pedda Konda	140, w; 240, w; 560, w; 920, m;	350, w; 670, w;

s=strong; m=medium; w=weak; and wB=weak Bulge.

as 11.8 per cent, these values indicate that the proportion of biotite is very large in these samples.

It may be mentioned here that basal reflection of this biotite is broad in nature extending from 10.2-11 Å and the intensity from its plane does not exactly reconcile with that of a well crystallized biotite. As a broadened basal reflection indicates interstratification in their lattice⁸, it may be expected that this biotite has been altered to some extent in the process to definite end-members, like chlorites and vermiculites⁹. As a result of this alteration, some interstratified layers are developed in the biotite lattice. Again, the reflection at 14.0 Å, indicates chlorite, vermiculite and/or montmorillonite but no characteristic peak of montmorillonite is observed in the thermograms (Fig. 1, Table 3). Hence this reflection is due to the presence of either chlorite or vermiculite or their mixture, and subsequently from the high order reflections both of these minerals have been identified in all these samples (Table 2).

Here again the intensities cannot be reconciled with those of vermiculite or magnesium chlorite. The reflection at 7.1 Å, which is identical in both the cases, does not appear in the x-ray diffraction pattern of these samples. Further, the interplanar spacings of both these minerals differ slightly from those of magnesium chlorite or vermiculite, and their DTA thermograms show endothermic peaks at 140-150, 240-250, 540-560 and 910-990°C and an exothermic bulge at 670-790°C (Fig. 1, Table 3). The initial and final endothermic peaks are characteristic of a vermiculite. But it is interesting to note that the initial endothermic peaks are immediately followed by one weak exothermic peak at about 310-380°C (Table 3), which may be due to oxidation of magnetite. However no evidence of the presence of magnetite has been found in their x-ray diffraction data (Table 2). The chemical analysis (Table 1) reveals the presence of Fe^{2+} ions to the extent of about 13 per cent as FeO . It may, therefore, be assumed that this peak is due to oxidation of Fe^{2+} ions which are present in the vermiculite structure and it may be inferred that such oxidation is only possible when the vermiculite structure is collapsed. The observed anomaly in the x-ray data of vermiculite which is present in these samples may, therefore, be accounted for by the presence of Fe^{2+} ions in their lattice.

Further, the peak at 540-560°C indicates presence of chlorite. But the characteristic peaks of magnesium chlorite—one endothermic peak at 800°C immediately followed by exothermic peak at 850°C are absent in these samples. Instead, the endothermic peak of chlorite (at about 550°C) is followed by a weak exothermic peak

at 670-790°C. According to Ivanova⁶, such a peak is possible in case of a highly ferruginous chlorite, known as thuringite. It is, therefore, quite possible that such a mineral exists in the Indian deposits also. The observed variation in the intensities as well as spacings of chlorite in their x-ray diffraction data may be accounted for as due to large incorporation of both Fe³⁺ and Fe²⁺ ions in the chlorite lattice. The chemical analysis (Table 1) also reveals that the samples are rich in both Fe³⁺ and Fe²⁺ ions (Fe₂O₃ 2.01-6.57 and FeO 1.91-12.81 per cent). Moreover, these peaks are not affected by the presence of other minerals, like biotite, as there is no peak in the thermogram of biotite upto 1000°C⁶.

The peak intensities are, however, found to vary from sample to sample indicating that the proportion of the constituent minerals for which these peaks are formed is not similar to one another. This indicates that alteration of biotite mica in these deposits is not uniform.

Acknowledgements

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Rock phosphate was treated with 10, 25, 50, 75 and 100 per cent of sulphuric acid required to convert it to a single superphosphate. These phosphate sources were applied in Sindri red soils contained in pots, for studying the yield and uptake of phosphorus by maize crop. It was found that with increased acidulation there were increases in uptake as well as yield; with acidulation at 50 per cent and above, the uptake and yield were very high, but when compared amongst themselves there was not much increase in uptake and also there was no significant increase in yield. Therefore, by adding half of the sulphuric acid required for single superphosphate manufacture, it is possible to economize the use of sulphuric acid and lower the cost of phosphate fertilization.

Various Concentrations of Sulphuric Acid-Treated Rock Phosphate as a Source of Phosphorus to Plants

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It is generally known that phosphorus recovery by plants from soils, treated with superphosphate during a growing season, does not exceed 25 per cent of the applied superphosphate. Kittrick and Jackson¹ have

shown that soils fixed phosphate at the rate of 100 tons of superphosphate/acre/hr. at the end of 3 min., but the

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rate has decreased to 1 lb/acre/hr. at the end of one month. MacIntire² et al and Mclean³ reported that Ca (H₂PO₄)₂. H₂O forms CaHPO₄, 2H₂O and phosphoric acid (H₃PO₄) in the soil. The phosphoric acid causes around the phosphate particle a solution having a pH 1.4, which is sufficiently acid to dissolve and displace large quantities of Al³⁺ and Fe³⁺. The above ions would be expected to precipitate the phosphates as AlPO₄ and FePO₄ and perhaps other even less soluble compounds⁴, and H⁺ ions remaining from H₃PO₄ could well displace or, activate still more Al³⁺ and Fe³⁺ which would depress the solubility of the relatively insoluble phosphate formed^{5,6}.

The efficiency and recovery of the available phosphorus from the partially acidulated material (with H₃PO₄) are apparently higher than when added alone⁷. According to Nordengreen⁸, the undecomposed apatite in a partially acidulated rock phosphate is being solubilized by the soil reactions. He also studied the condition for maximum solubilization in which rock phosphate was thoroughly and rapidly mixed with half the amount of sulphuric or phosphoric acid ordinarily used in making superphosphates, so that each particle of rock received a coating of available phosphate.

Several attempts to economize the cost of phosphate fertilization were carried out by combining soluble and insoluble (rock phosphate) phosphate materials, or by using less acid than the amount required to convert all the tricalcium phosphate into mono-calcium phosphate^{9,10}. In general, the mixing of appreciable amounts of soluble with insoluble forms of phosphate has decreased the availability of the less soluble material¹¹. However, several reports have indicated that 50:50 mixtures of rock phosphate and superphosphate or, 50 per cent acidulated rock phosphates are as effective as equivalent amounts of superphosphate.

Indian soils contain appreciable quantities of phosphorus-fixing ions and they can fix as high as 30 mg. of P₂O₅/100 g. soil (i.e. 600 lbs./acre), as in the case of Sindri red soil (Table 1), which fixes almost immediately the whole amount¹². It was, therefore, necessary to study the availability and uptake of phosphorus from various proportions of sulphuric acid-treated rock phosphate with a view to economizing the use of the acid, thus decreasing the cost of fertilization and also getting the best return at a minimum cost.

Materials and Method

Rock phosphate was acidulated with 0, 10, 25, 75, and 100 per cent of sulphuric acid required to convert it into single superphosphate. Each fertilizer was pre-

TABLE 1—ANALYSIS OF SINDRI RED SOIL
[Oven-dry basis]

(A) Mechanical Analysis %			
Clay	..	..	29
Silt	..	..	5
Sand		..	58
(B) Chemical Analysis			
Organic Carbon, %	..	..	0.37
Total Nitrogen, %	..	..	0.04
Total P ₂ O ₅ , %	..	..	0.07
Total K ₂ O, %	..	..	1.46
pH	..	..	6.65
C.E.C., m. eq/100 g. soil	..	..	12.60

pared by adding the acid slowly to the rock phosphate, which was previously ground and passed through a 100 mesh (B.S.S.) sieve, and mixing the ingredients continuously and thoroughly for ½ hr. The mixtures were allowed to stand for 6 hr. and then dried in an oven at 70°C. The chemical analyses of the Jordan rock phosphate sample used and the rock phosphates acidulated with different proportions of the acid are given in Tables 2 and 3 respectively.

TABLE 2—ANALYSIS OF JORDAN ROCK PHOSPHATE, % BY WT.

CaO	..	..	52.40
P ₂ O ₅	..	..	34.45
F ₂	..	..	5.68
CO ₂	..	..	4.75
SO ₃	..	..	Traces
SiO ₂	..	..	2.50
R ₂ O ₃	..	..	0.22
MgO	..	..	Nil

TABLE 3—CHEMICAL ANALYSIS OF ACIDULATED ROCK PHOSPHATE

Sl. No.	Acidulation, % by weight	Citrate-Soluble P ₂ O ₅ , %	Total Available (Citrate-soluble + Water-soluble) P ₂ O ₅ , %	Total Water-soluble P ₂ O ₅ , %	Total P ₂ O ₅ , %
1.	0 i.e. R.P.	2.99	2.99	Nil	34
2.	10	4.55	4.60	0.05	30
3.	25	4.83	6.37	1.54	29
4.	50	6.65	12.88	6.23	21.2
5.	75	2.99	16.10	13.11	19.2
6.	100	0	15.9	15.9	15.9

These sulphuric acid-treated rock phosphates together with a blank (with no. N, P or K) and a control (N and K only) were included as treatments. Each phosphate material was added to the soil at the rate of 200 lbs. of total P_2O_5 /acre. Nitrogen and potash (K_2O) were added uniformly at the rate of 50 lbs./acre obtained from ammonium sulphate and potassium chloride, respectively. The phosphates were applied to 100 kg. portions of Sindri red soil (Table 1) in stoneware glazed pots at 2½-3in. below the surface.

All the treatments were made in quadruplicate with the pots arranged in a completely randomized design. The maize seeds were planted in uniformly spaced positions in the pots. After the appearance of seedlings they were thinned to 10 maize plants/pot. The plants were harvested after one month near the surface of the soil. The plant materials were dried in an oven at 70°C weighed and ground. 1g. of the ground material was digested in a tri-acid mixture and their phosphorous content determined colorimetrically by the vanadomolybdate method¹³. The results are given in Table 4.

TABLE 4

Treatment	Dry Weight of the plant, g./pot (Average of 4 replications)	Phosphorus Uptake, mg./pot (Average of 4 replications)
Blank (0-0-0)	4.28	6.56
Control (50-0-50)	5.34	9.94
R.P. (50-200-50)	5.87	11.25
10% Acidulation (50-200-50)	6.65	11.23
25% Acidulation (50-200-50)	9.59	15.53
50% Acidulation (50-200-50)	13.11	30.40
75% Acidulation (50-200-50)	13.83	36.90
100% Acidulation (50-200-50)	14.08	30.26
C.D. 5%	1.43	5.07

Results and Discussion

From Fig. 1 it is apparent that with increase in acidulation, the mean dry weight (g./pot) of the plant also increased upto 50 per cent acidulation beyond which there was no appreciable increase. It also shows the

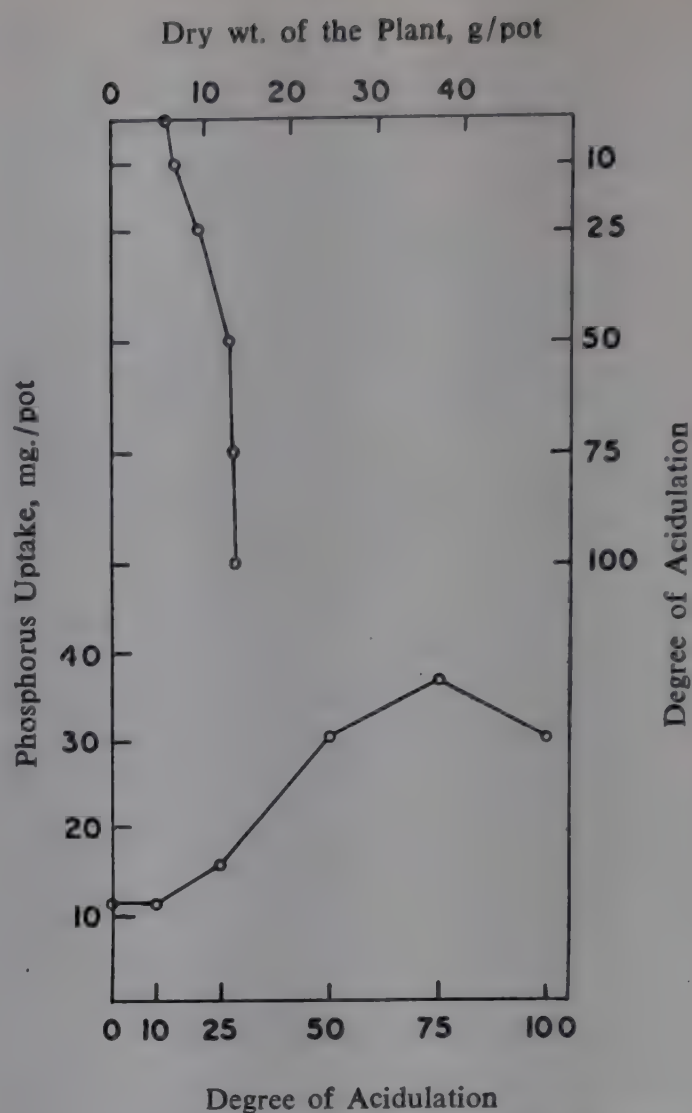


Fig. 1—Dry Matter Yield and Phosphorous uptake by Maize

mean phosphorus uptake (mg./pot) increases as the degree of acidulation increases. It is seen that upto 10 per cent acidulation there was no increase, after which it increased upto 75 per cent acidulation. At 100 per cent acidulation, i.e. on the formation of single superphosphate the P_2O_5 uptake decreased. The P_2O_5 uptake increased appreciably upto 50 per cent acidulated rock phosphate after which at 75 per cent level the increase in uptake was very little.

With increase in acidulation, the available P_2O_5 also increases (Table 3), and this may be the reason for more increased dry matter yield and phosphorus uptake.

At higher acidulation than 50 per cent, the water-soluble P_2O_5 (mostly monocalcium phosphate) increases, whereas the citrate-soluble P_2O_5 decreases. In the case of 100 per cent acidulation all the P_2O_5 is in water-soluble form and may have hydrolysed, when placed in soil, forming H_3PO_4 . The H_3PO_4 , thus produced, possibly reacts with Fe^{3+} and Al^{3+} present in the soil to form slightly soluble phosphate compounds. This may account for the decrease in phosphorus uptake by the plants in case of 100 per cent acidulation treatment.

A statistical analysis of the results (Table 4) shows that the variations in the plant yields and phosphorus uptake due to various rock phosphate treatment were significant at 1 per cent level of significance.

It is to be noted, however, that P_2O_5 uptake increases appreciably upto 50 per cent acidulation and then remains almost constant upto 100 per cent acidulation with a slight increase in uptake around 75 per cent, but there is no significant difference in mean dry weight of the plant when compared amongst themselves. It can be concluded that by using half the acid (i.e. 50 per cent) required for single superphosphate, the use of sulphuric acid can be economized, and thus lower the cost of the phosphate fertilizer.

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Structures of two forms of copper-biuret complex have been established as square planar from the study of optical and ESR spectra. The coordination is with four nitrogens, as found from hyperfine splittings in the ESR spectra. Optical absorption bands at 18690, 30303 and 34364 cm^{-1} for the purple and at 19380, 31250 and 38460 cm^{-1} for the red complex have been observed in solution. Respective g-values are 2.0902 and 2.0939. Overlap coefficients have been calculated.

ESR and Optical Studies on Copper-Biuret Complexes

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The importance of detection, estimation and control of the concentration of biuret during the production of urea is well known. Colorimetric methods of estimation of biuret have been evolved taking advantage of the coloured complexes that it forms with different transition metal ions, the purple coloured copper-biuret com-

plex being the earliest one to be employed. But there seems to be a lot of confusion about the structure of this familiar complex. Kato¹ et al. had proposed that the structure of this complex was planar, copper being four-coordinated with two nitrogens of the biuret and two hydroxyl groups. A more recent work by McLellan and

Melson² also supports Kato's idea in the main, they further postulate that there is a dimeric association in the complex, the hydroxyl groups serving as bridges between two copper ions, between whom an antiferromagnetic bond is postulated to exist in order to explain the abnormally small magnetic moment observed by Melson³. Copper is stated to be hexacoordinated. Freeman⁴ et al, on the other hand, had investigated the structure of the purple complex by x-ray crystallographic methods and had come to the conclusion that each Cu ion is coordinated with two biuret molecules through four nitrogens, the coordination being essentially square planar.

Two more modifications of the complex are known to exist, one a pale green cationic hexacoordinated complex²⁻⁶ studied by both Freeman and McLellan, and the other, a red coloured complex reported by the latter², and assumed to be hexacoordinated also, to two biuret groups and two nitrogens from other biuret groups.

The present work aims at resolving the obvious inconsistencies between the findings of Freeman and McLellan on the purple copper-biuret complex and also to elucidate the structure of the two other forms mentioned above. The optical spectra of the purple and red complexes are discussed from the point of view of the symmetry of their structures and ESR spectra are studied to identify the ligands through the hyperfine interaction of the unpaired copper 3d electron with the ligand nuclei. The pale green complex is studied for the sake of completeness.

Part I—The Optical Absorption Spectra

Experimental

The red and the purple forms of the copper-biuret complex were prepared according to the method given by McLellan. The amount of alcohol added was reduced to inhibit crystallization. For the spectrophotometric studies, the dilutions were achieved by KOH solutions of the appropriate pH.

The optical absorption spectra of the complexes were studied by a Beckman DU-2 Spectrophotometer. The spectra are reproduced in Fig. 1. It may be observed that the spectra of the two forms are very similar, each comprising three peaks, only the peak positions are shifted somewhat relative to one another. The spectrum of biuret alone, dissolved in an aqueous solution of KOH maintained at pH 11.3 was also taken to ensure that none of the peaks observed in the spectra of the complex was due to free biuret.

Let us now critically examine the alternative structures for the purple complex as proposed by McLellan

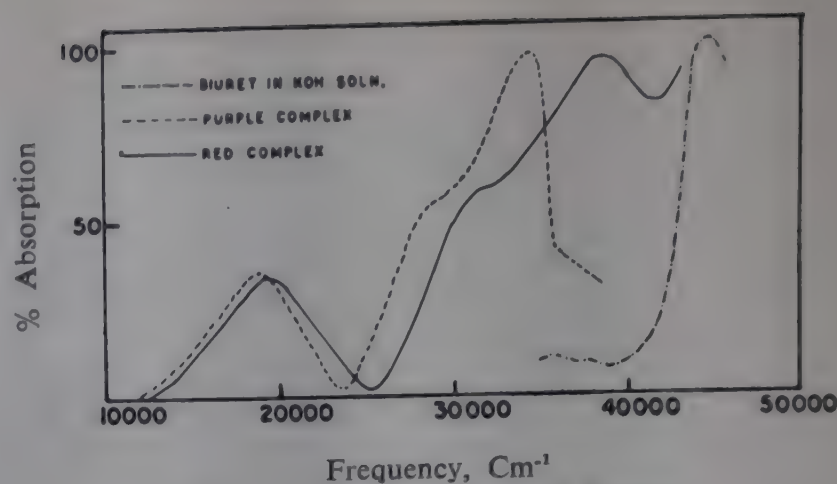


Fig. 1—Optical Absorption Spectra

on the one hand and Freeman on the other, and discuss the nature of the absorption spectrum arising from each of them.

If we assume a six-coordinated Cu^{2+} ion following McLellan, incorporating two OH groups, the resultant configuration of ligands around the Cu^{2+} ion is shown in Fig. 2.

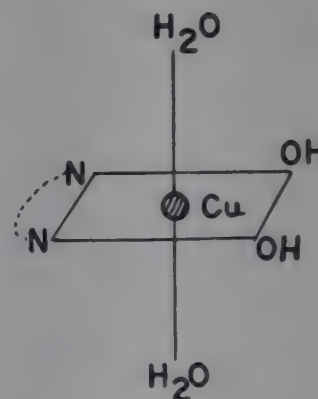


Fig. 2—Symmetry proposed by McLellan & Melson

The symmetry of this structure is C_2 , the two-fold axis passing through the copper perpendicular to the $\text{H}_2\text{O}-\text{Cu}-\text{H}_2\text{O}$ axis and bisecting the $\text{N}-\text{Cu}-\text{N}$ angle. The symmetry is not altered if the two OH groups are replaced by H_2O in the solution state as assumed by McLellan.

The electronic state of the $d^9 \text{Cu}^{2+}$ ion is conveniently described by the single d-hole formalism which holds equally well for all ligand field strengths. The character table for the C_2 symmetry group is shown below, with the character of the representation for the d wave function indicated by Γ .

	E	C_2
A	1	1
B	1	-1
Γ	5	1

The break-up of this reducible representation into its irreducible components is obviously
 $\Gamma = A + A + A + B + B$

The energy level thus splits into five orbitally non-degenerate levels, each with a twofold spin degeneracy. As there is no centre of symmetry, no question of parity restriction arises for the d→d transitions and the expected absorption spectrum should contain four prominent bands for such transitions. Knowing the band positions for octahedral complexes⁷ with H₂O and NH₃, we may expect an absorption maximum around 14000 cm⁻¹ with four fine-structure lines in the absorption spectrum of this complex.

Next, the structure proposed by Freeman is considered in somewhat greater detail. Here the coordination is through four nitrogen atoms belonging to two biuret groups. The local symmetry at the central Cu²⁺ ion may be taken as D_{4h}. In this case a centre of inversion is present and the wave functions may be classified according to their parity. The molecular orbitals formed according to hybrid orbital scheme^{8,9} are

$$\begin{aligned}
 |B_{1g}\rangle &= a_1 |d_{x^2-y^2}\rangle + \frac{b_1}{2} (-|p_{x1}\rangle + |p_{y2}\rangle + |p_{x3}\rangle - |p_{y4}\rangle) \\
 |A_{1g}\rangle &= a_2 (m |s\rangle + n |d_{z^2}\rangle) + \frac{b_2}{2} (|h_1\rangle + |h_2\rangle + |h_3\rangle + |h_4\rangle) \\
 &\quad (\text{where } m^2 + n^2 = 1) \\
 |E_g\rangle &= \begin{cases} a_3 |d_{zx}\rangle + \frac{b_3}{\sqrt{2}} (|p_{z1}\rangle - |p_{z3}\rangle) \\ a_3 |d_{yz}\rangle + \frac{b_3}{\sqrt{2}} (|p_{z2}\rangle - |p_{z4}\rangle) \end{cases} \\
 |B_{2g}\rangle &= a_4 |d_{xy}\rangle + \frac{b_4}{2} (|p_{y1}\rangle + |p_{x2}\rangle - |p_{y3}\rangle - |p_{x4}\rangle) \\
 |A_{2u}\rangle &= a_5 |p_z\rangle + \frac{b_5}{2} (|p_{z1}\rangle + |p_{z2}\rangle + |p_{z3}\rangle + |p_{z4}\rangle) \\
 |E_u\rangle &= \begin{cases} a_6 |p_x\rangle - \frac{b_6}{\sqrt{2}} (|p_{x1}\rangle + |p_{x3}\rangle) \\ a_6 |p_y\rangle - \frac{b_6}{\sqrt{2}} (|p_{y2}\rangle + |p_{y4}\rangle) \dots \end{cases} \quad (1)
 \end{aligned}$$

The ligand positions are designated by the numbers 1 to 4, as follows:

$$\begin{aligned}
 (a,0,0) &\equiv 1 \\
 (0,a,0) &\equiv 2 \\
 (-a,0,0) &\equiv 3 \\
 (0,-a,0) &\equiv 4
 \end{aligned}$$

$|p_{x1}\rangle$ denotes the positive x-lobe of the 2p orbital of the ligand in position 1, and similarly for the other ligand orbitals. The unnumbered wave functions denote the copper atomic orbitals. The functions $|h_i\rangle$ are ligand 2s-2p hybrids given by

$$\begin{aligned}
 |h_1\rangle &= r |s_1\rangle - t |p_{x1}\rangle \\
 |h_2\rangle &= r |s_2\rangle - t |p_{y1}\rangle \\
 |h_3\rangle &= r |s_3\rangle + t |p_{x3}\rangle \dots \dots (2) \\
 |h_4\rangle &= r |s_4\rangle + t |p_{y4}\rangle
 \end{aligned}$$

where $r^2 + t^2 = 1$

The coefficients a_i , b_i in expressions (1) are to be evaluated as follows:

$$\begin{aligned}
 |\Psi_i\rangle &= a_i |\Psi_{i\text{metal}}\rangle + b_i |\Psi_{i\text{ligand}}\rangle \\
 \langle \Psi_i | \Psi_j \rangle &= a_i^* a_j \langle \Psi_{i\text{met}} | \Psi_{j\text{met}} \rangle + \\
 &\quad b_i^* b_j \langle \Psi_{i\text{lig}} | \Psi_{j\text{lig}} \rangle + \\
 &\quad + a_i^* b_j \langle \Psi_{i\text{met}} | \Psi_{j\text{lig}} \rangle + \\
 &\quad b_i^* a_j \langle \Psi_{i\text{lig}} | \Psi_{j\text{met}} \rangle = \delta_{ij}
 \end{aligned}$$

where $\delta_{ij} = 1$ or 0 according as $i=j$ or $i \neq j$

Therefore for real coefficients

$$a_i^2 + b_i^2 + 2a_i b_i S_i = 1$$

where $S_i = \langle \Psi_{i\text{met}} | \Psi_{i\text{lig}} \rangle$ is the overlap between the metal and ligand wave functions. The expressions in (1) are for the bonding orbitals. For the antibonding orbitals a_i and b_i have to be interchanged and the signs of the ligand functions are to be reversed.

To evaluate the matrix elements of the ligand field energy operator, we note that the operator must be invariant under all the symmetry operations of the substitution group, i.e. it belongs to the representation A_{1g}. Therefore non-zero matrix elements will be obtained only between wave functions belonging to the same irreducible representation. It should be stressed that the operator equivalent method developed by Elliot & Stevens¹⁰ and Judd¹¹ is not applicable in the case of molecular orbitals, as the method is restricted to single orbital manifolds, i.e. where the orbital quantum number L is same for all the wave functions. Therefore, we shall have to express both the ligand field operator and the angular part of the wave functions in terms of spherical harmonics Y_l^m and compute the matrix elements by using the Clebsch-Gordan coefficients (also known as Wigner coefficients). We intend to outline the procedure in some detail as the necessary material is found only in a scattered manner in literature.

The different wave functions involved are given below (Table 1). The functions are expressed as products of a radial function R_{n,l} and an angular function Y_l^m(θ,φ), the latter being a spherical harmonic, each normalized separately.

TABLE 1

Atomic Orbital	Form of the Function	Atomic Orbital	Form of the Function
$3d_z^2$	$R_{3,2} Y_2^0$	$4s$	$R_{4,0} Y_0^0$
$3d_{zx}$	$R_{3,2} \frac{Y_2^1 + Y_2^{-1}}{\sqrt{2}}$	$2s$	$R_{2,0} Y_0^0$
$3d_{yz}$	$R_{3,2} \frac{Y_2^1 - Y_2^{-1}}{\sqrt{2}i}$	$2p_z$	$R_{2,1} Y_1^0$
$3d_{x^2-y^2}$	$R_{3,2} \frac{Y_2^2 + Y_2^{-2}}{\sqrt{2}}$	$2p_x$	$R_{2,1} \frac{Y_1^1 + Y_1^{-1}}{\sqrt{2}}$
$3d_{xy}$	$R_{3,2} \frac{Y_2^2 - Y_2^{-2}}{\sqrt{2}i}$	$2p_y$	$R_{2,1} \frac{Y_1^1 - Y_1^{-1}}{\sqrt{2}i}$

The form of the potential function at the point (r, θ, ϕ) , assuming an ionic model where four charges Ze' each located at $(\pm a, 0, 0)$ and $(0, \pm a, 0)$ can be shown¹² to be

$$V = KZe' \sqrt{\pi} \left[-\frac{4}{\sqrt{5}} \frac{r^2}{a^3} Y_2^0 + \frac{r^4}{a^5} \left\{ Y_4^0 + \frac{\sqrt{70}}{6} (Y_4^4 + Y_4^{-4}) \right\} \right] \dots (3)$$

In the molecular orbital model, the symmetry of the potential remains unaltered. Thus the same spherical harmonics will be used here also, although Ze' will differ for different orbitals.

Therefore integrals of the type $\int \int \bar{Y}_{l_2}^{m_2} Y_{l_1}^m Y_{l_1}^{m_1} \sin \theta d\theta d\phi$ will have to be evaluated. Now, the spherical harmonic functions Y_l^m may be regarded as the basis for a $(2l+1)$ -dimensional irreducible representation of the rotation group and hence the products $Y_l^m Y_{l_1}^{m_1}$ form the basis of the direct product of the respective representations. Decomposing the direct product into its irreducible components, we shall get a fresh set of basis functions $Y_l^{m'}$ with $|l-l_1| \leq l' \leq l+l_1$ and $m'=m+m_1$ according to the relation¹².

$$Y_l^m Y_{l_1}^{m_1} = \frac{1}{2\sqrt{\pi}} \sum_{l'=|l-l_1|}^{l+l_1} \sqrt{\frac{(2l+1)(2l_1+1)}{2l'+1}} (ll_1 mm_1 | l'm') (ll_1 00 | l'0) Y_{l'}^{m'} \dots (4)$$

where $(ll_1 mm_1 | l'm')$ and $(ll_1 00 | l'0)$ are the Clebsch-Gordan coefficients. For non-vanishing matrix elements, we need retain only the term for which $m'=m_2$ and $l'=l_2$.

The general expression for the Clebsch-Gordan coefficient is $(l_1 l_2 m_1 m_2 | l m) =$

$$\left[\frac{2l+1}{l_1+1+l_2+1} (l_2+l-l_1)! (l+l_1-l_2)! (l_1+l_2-l)! (l_1+m_1)! (l_1-m_1)! (l_2+m_2)! (l_2-m_2)! (l+m)! (l-m)! \right]^{\frac{1}{2}} \frac{(-1)^z}{z! (l_1+l_2-l-z)! (z+l-l_1-m_2)! (l_2+m_2-z)!} \frac{1}{(z+l-l_2+m_1)! (l_1-m_1-z)!}$$

where z takes all non-negative integer values consistent with the factorials. The values of the relevant coefficients are given in Table 2.

TABLE 2

$(2000 20)$	$= 2 \sqrt{6}$	$(2202 22)$	$= 12 \sqrt{10/7}$
$(2100 10)$	$= -4 \sqrt{3/5}$	$(220-2 2-2)$	$= 12 \sqrt{10/7}$
$(2101 11)$	$= 2 \sqrt{3/5}$	$(4200 20)$	$= 48 \sqrt{5}$
$(210-1 1-1)$	$= 2 \sqrt{3/5}$	$(4201 21)$	$= -32 \sqrt{5}$
$(2100 20)$	$= 0$	$(420-1 2-1)$	$= -32 \sqrt{5}$
$(2200 00)$	$= 2 \sqrt{6/5}$	$(4202 22)$	$= 8 \sqrt{5}$
$(2200 10)$	$= 0$	$(420-2 2-2)$	$= 8 \sqrt{5}$
$(2200 20)$	$= -12 \sqrt{10/7}$	$(424-2 22)$	$= 40 \sqrt{14}$
$(2201 21)$	$= -6 \sqrt{10/7}$	$(42-42 2-2)$	$= 40 \sqrt{14}$
$(220-1 2-1)$	$= -6 \sqrt{10/7}$		

The integrals of the relevant triple products of normalized spherical harmonics which are required for evaluating the matrix elements of V are calculated, utilizing the values given in Table 2 and are listed in Table 3. The integrals are of the form:

$$\int_{\theta=-\pi}^{\pi} \int_{\phi=0}^{2\pi} \bar{Y}_{l_2}^{m_2}(\theta, \phi) Y_{l_1}^{m_2-m_1}(\theta, \phi) Y_{l_1}^{m_1}(\theta, \phi) \sin \theta d\theta d\phi$$

where $|l_2-l_1| \leq l \leq l_2+l_1$. Only two values of l , viz. 2 and 4 need be considered. The symbol $d\gamma$ is used in the table as an abbreviation for $\sin \theta d\theta d\phi$.

Table 3

$\int \bar{Y}_2^0 Y_2^0 Y_0^0 d\gamma$	$=$	$12/\sqrt{5\pi}$
$\int \bar{Y}_1^0 Y_2^0 Y_1^0 d\gamma$	$=$	$24/\sqrt{5\pi}$
$\int \bar{Y}_1^1 Y_2^0 Y_1^1 d\gamma$	$=$	$-12/\sqrt{5\pi}$
$\int \bar{Y}_1^{-1} Y_2^0 Y_1^{-1} d\gamma$	$=$	$-12/\sqrt{5\pi}$
$\int \bar{Y}_2^0 Y_2^0 Y_2^0 d\gamma$	$=$	$\frac{720}{7} \sqrt{\frac{5}{\pi}}$
$\int \bar{Y}_2^1 Y_2^0 Y_2^1 d\gamma$	$=$	$\frac{360}{7} \sqrt{\frac{5}{\pi}}$
$\int \bar{Y}_2^{-1} Y_2^0 Y_2^{-1} d\gamma$	$=$	$\frac{360}{7} \sqrt{\frac{5}{\pi}}$
$\int \bar{Y}_2^2 Y_2^0 Y_2^2 d\gamma$	$=$	$-\frac{720}{7} \sqrt{\frac{5}{\pi}}$
$\int \bar{Y}_2^{-2} Y_2^0 Y_2^{-2} d\gamma$	$=$	$-\frac{720}{7} \sqrt{\frac{5}{\pi}}$

$$\begin{aligned}
\int \bar{Y}_3^0 Y_4^0 Y_3^0 d\gamma &= 17280/\sqrt{\pi} \\
\int \bar{Y}_3^1 Y_4^0 Y_3^1 d\gamma &= -11520/\sqrt{\pi} \\
\int \bar{Y}_3^{-1} Y_4^0 Y_3^{-1} d\gamma &= -11520/\sqrt{\pi} \\
\int \bar{Y}_3^2 Y_4^0 Y_3^2 d\gamma &= 2880/\sqrt{\pi} \\
\int \bar{Y}_3^{-2} Y_4^0 Y_3^{-2} d\gamma &= 2880/\sqrt{\pi} \\
\int \bar{Y}_3^2 Y_4^1 Y_3^{-1} d\gamma &= 2880\sqrt{\frac{70}{\pi}} \\
\int \bar{Y}_3^{-2} Y_4^{-1} Y_3^2 d\gamma &= 2880\sqrt{\frac{70}{\pi}}
\end{aligned}$$

In the above, $\bar{Y}_l^m$ is to be interpreted as the complex conjugate of Y_l^m , and $\bar{Y}_l^m = Y_l^m$

The matrix elements of the potential V in eqn. (3) are calculated by using these values. Remembering that

$$\langle d_{xy} | = \left\{ \frac{1}{\sqrt{2i}} (Y_2^2 - Y_2^{-2}) \right\}^* = -\frac{1}{\sqrt{2i}} (Y_2^{-2} - Y_2^2) = \frac{1}{\sqrt{2i}} (Y_2^2 - Y_2^{-2}) \text{ and similar relations for the other functions}$$

$$\langle B_{1g} | V | B_{1g} \rangle = 36480 a_1^2 c \frac{\bar{r}^4}{a^4} + (411.43 a_1^2 + 9.6 b_1^2) c' \frac{\bar{r}^2}{a^2}$$

$$\langle A_{1g} | V | A_{1g} \rangle = 17280 a_2^2 n^2 c \frac{\bar{r}^4}{a^4} - (411.43 a_2^2 n^2 + 19.2 a_2^2 m n - 9.6 b_2^2 t^2) c' \frac{\bar{r}^2}{a^2}$$

$$\langle E_g | V | E_g \rangle = -11520 a_3^2 c \frac{\bar{r}^4}{a^4} - (205.7 a_3^2 + 19.2 b_3^2) c' \frac{\bar{r}^2}{a^2}$$

$$\langle B_{2g} | V | B_{2g} \rangle = -30720 a_4^2 c \frac{\bar{r}^4}{a^4} + (411.43 a_4^2 + 9.6 b_4^2) c' \frac{\bar{r}^2}{a^2}$$

$$\text{where } c = \frac{K Z e'}{a} \text{ and } c' = \frac{K Z' e'}{a}$$

$Z e'$ and $Z' e'$ being the effective charges for the 4th and 2nd order terms, respectively in the potential expression.

$\bar{r}^4$ and $\bar{r}^2$ are defined by

$$\bar{r}^m = \int_0^\infty R_{n,l}^* r^m R_{n,l} r^2 dr \text{ for } R_{n,l} \text{ normalized to } \int_0^\infty R_{n,l}^* R_{n,l} r^2 dr$$

Remembering that we are dealing with a positive hole in the 3d shell of Cu and that the ligands, according to the structure given by Freeman, are N^- ions, energetically the B_{1g} level comes the lowest, then come the A_{1g} , E_g and B_{2g} , in that order.

In order to compare with the actual spectrum observed we introduce certain simplifications and approximations:

Firstly, we observe that in the bonding orbitals, $b_1 \ll a_1$, and that the coefficients of the b_1^2 terms in the energy expression are much smaller in comparison with the other terms. Therefore, we can neglect the contribution from the b_1^2 terms, i.e. the ligand terms, without incurring any appreciable error. The a_2^2 mn term in

$\langle A_{1g} | V | A_{1g} \rangle$ is also neglected on similar grounds.

Secondly, we assume that $(\bar{r})^m = (\bar{r}^m)$ and that $\bar{r}$ = the ionic radius for Cu^{2+} approximately. It is a justified simplification in view of the fact that the coefficient of $\bar{r}^2$ is smaller by two orders of magnitude than the coefficient of $\bar{r}^4$.

Thirdly, we write $Z' = Z$ as an approximation. With these in mind, and putting $e' = -e$ where $-e$ is the electronic charge, the energy expressions are:

$$\begin{aligned}
E(B_{1g}) &= -A \left[36480 \left(\frac{\bar{r}^2}{a} \right) + 411 \right] a_1^2 \\
E(A_{1g}) &= -A \left[17280 \left(\frac{\bar{r}^2}{a} \right) - 411 \right] a_2^2 n^2 \\
E(E_g) &= A \left[11520 \left(\frac{\bar{r}^2}{a} \right) + 206 \right] a_3^2 \dots (5) \\
E(B_{2g}) &= A \left[30720 \left(\frac{\bar{r}^2}{a} \right) - 411 \right] a_4^2
\end{aligned}$$

$$\text{where } A = K Z e^2 \frac{\bar{r}^2}{a^3}$$

Now taking the value $a = 1.95 \text{ \AA}$ from Freeman and taking the radius of nitrogen¹⁴ as $0.75 \text{ \AA}$, we obtain

$$\begin{aligned}
E(B_{1g}) &= -8964 A a_1^2 \\
E(A_{1g}) &= -4462 A a_2^2 n^2 \\
E(E_g) &= 2907 A a_3^2 \\
E(B_{2g}) &= 6761 A a_4^2
\end{aligned}$$

We can evaluate the $A a_1^2$ by utilizing the frequencies of the three absorption peaks and the relation of the conservation of the centre of gravity of the original level. The values thus calculated are given in Table 4.

TABLE 4

Complex	$A a_1^2$	$A a_2^2 n^2$	$A a_3^2$	$A a_4^2$
Purple	2.538 cm ⁻¹	0.9103 cm ⁻¹	2.597 cm ⁻¹	1.865 cm ⁻¹
Red	2.688 cm ⁻¹	1.004 cm ⁻¹	2.471 cm ⁻¹	2.128 cm ⁻¹

As it may be observed from Fig. 1, the spectra of the two compounds are of identical nature, so that the same

ligand field symmetry can be ascribed to the Cu^{2+} ion site for both the complexes. The overlap coefficients a_1, a_2, a_3, a_4 are found to be of quite similar values as may be expected. The $Aa_2^2 n^2$ term is understandably smaller because of the presence of the n^2 factor arising from the admixture of the copper $3d_{z^2}$ and $4s$ orbitals. Assuming identical values for a_1 and a_2 , the values of n are found to be 0.5989 and 0.6112 respectively for the purple and the red complex.

The differences in the Aa_1^2 terms observed arise also from the different effective Z values for the different orbitals, so that with the available data, it is not possible to calculate the overlap coefficients to any greater detail.

Even assuming no orbital overlap, i.e. with $a_1=a_2=a_3=a_4=1$, the general nature of the calculated spectrum agrees well with the observed spectra, the frequency of the first absorption peak, arising from the transition $B_{1g} \rightarrow A_{1g}$, being nearly half that of the second peak due to $B_{1g} \rightarrow E_g$. The third peak $B_{1g} \rightarrow B_{2g}$ is expected somewhat closer, as observed experimentally. However, it is possible that the observed *peak* is the combined effect of a charge transfer band and the $d \rightarrow d$ transition, as the peak differs only slightly in position for the two complexes, and as its intensity is so high. Of course, for strongly covalent complexes, $d \rightarrow d$ transitions and charge transfer cannot be sharply distinguished.

For an octahedral coordination with the degree of tetragonal distortion usually associated with copper complexes, the B_{2g} level and the A_{1g} level are interchanged in their relative positions, and the splitting between the B_{1g} and B_{2g} levels is much less, so that the relative spacings between the levels are altered. The observed spectrum then can be roughly interpreted as arising from the transition between the cubic E_g and T_{2g} levels, with the anisotropic splittings usually unresolved.

Therefore, from the optical spectrum we confirm the coordination of the Cu^{2+} ion to be square planar, both in the purple as well as in the red complex.

Part II—ESR Spectra

Experimental

The ESR spectra of all the three different forms of the Cu-Biuret Complex were studied both in the solid and the solution state, on a Bruker Model B-ER 402 X-Band ESR Spectrometer. The magnetic field was measured by a proton resonance gaussmeter and the g -values measured using polycrystalline DPPH as reference ($g=2.0036$). The solutions were studied by taking them in thin-walled pyrex glass capillaries which were

previously tested to ensure that they gave rise to no spurious signals.

The spectra for the solutions are reproduced in Fig. 3 and those for the solids in Fig. 4.

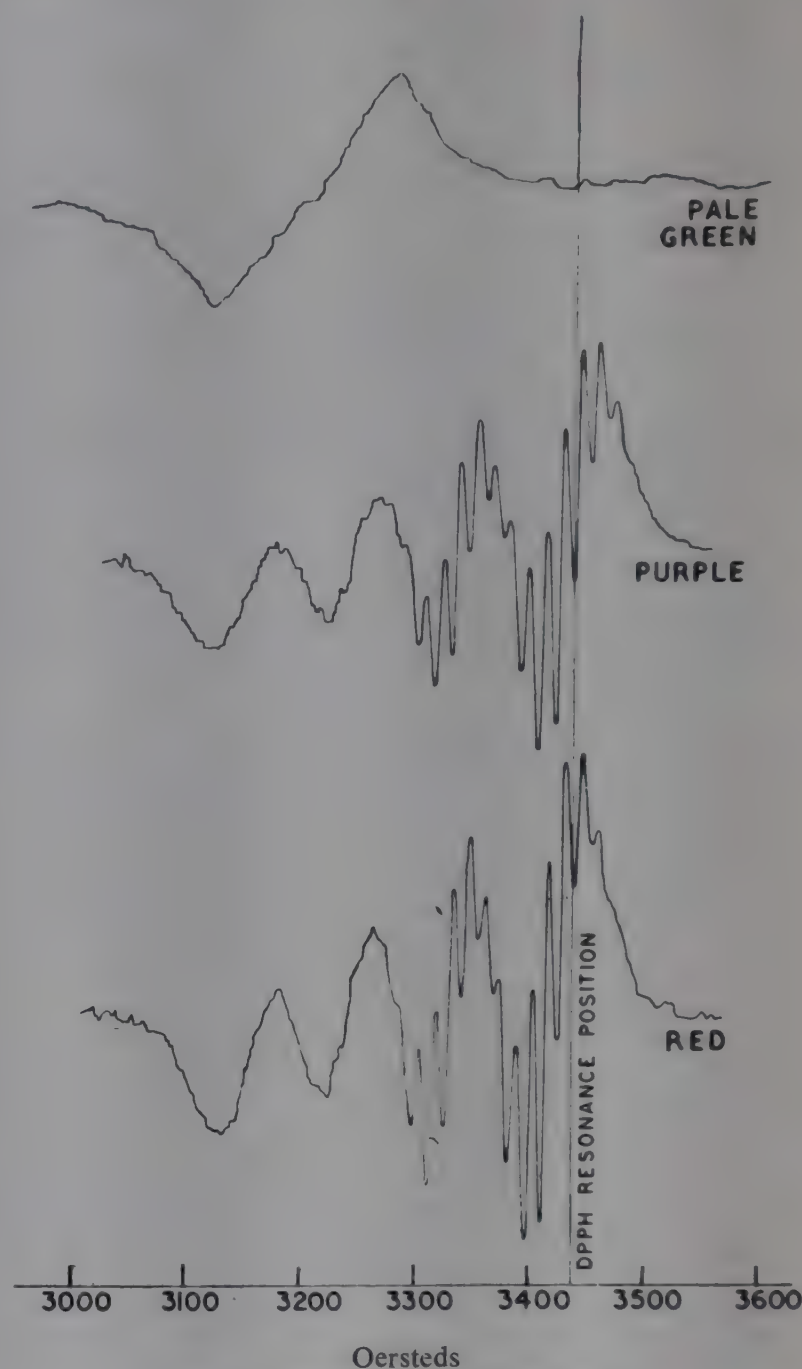


Fig. 3—ESR Spectra of Solutions

It is observed that both the red and the purple complexes give rise to almost identical spectra, showing four hyperfine lines due to copper ($I=\frac{3}{2}$) and super-hyperfine splittings due to interaction with the nitrogen nuclei. The spectra are almost similar to the spectrum of copper etioporphyrine observed by Roberts and Kosky¹⁵, where Cu^{2+} is known to be coordinated to four nitrogen nuclei in a square planar configuration.

The spacings of the copper-hyperfine lines are not uniform. For the red complex, the separation between the centres of the first and second lines (counting from the lower magnetic field end) is 93.96 oersteds, that

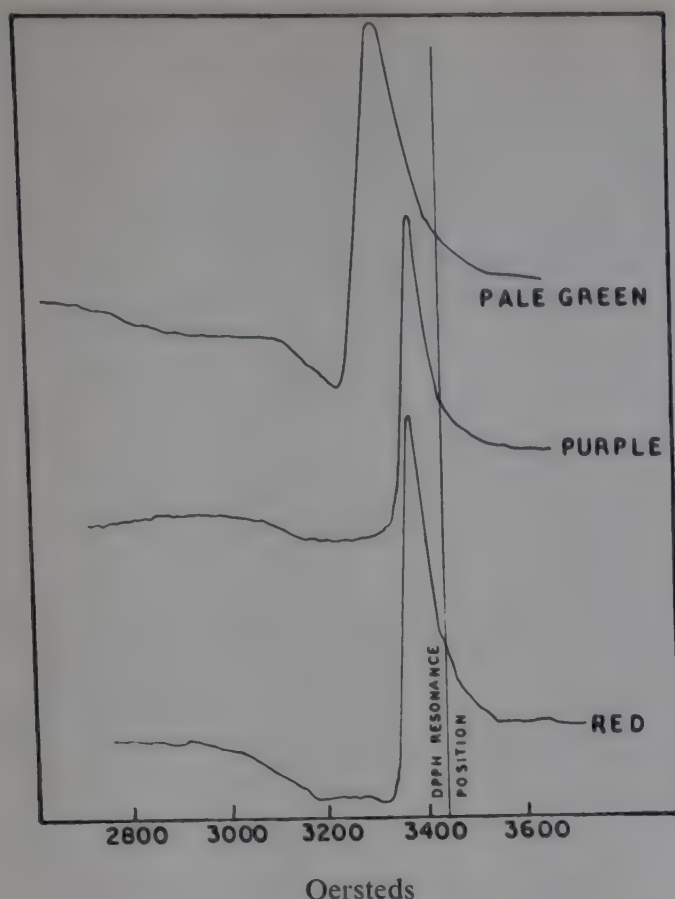


Fig. 4—ESR Spectra of Solid Samples

between the second and third is 87 oersteds, and between the third and fourth a separation of 90.3 oersteds is observed. The values are somewhat greater in the case of the purple complex.

There are seven nitrogen hyperfine lines observed on the fourth ($I_z = \frac{3}{2}$) copper line, five on the third and a trace of three lines on the second. The splitting due to nitrogen is observed to be 15.58 oersteds, i.e. the coupling of the unpaired electron is of the same order as observed in DPPH. The theoretically expected pattern of the hyperfine splitting due to four nitrogen nuclei comprises nine lines with the intensity ratio 1:4:10:16:19:16:10:4:1. The experimentally observed seven line pattern was interpreted by Roberts and Kosky¹⁵ as due to the low intensity of the extreme lines.

The pale green sample shows no nitrogen hyperfine splitting substantiating the contention that in this case, the bonding is through oxygens.

Calculations

(A) *g-Values*: The spin-Hamiltonian, neglecting the nuclear quadrupole interaction term is given by

$$H_S = \sum_{ij} [\beta g_{ij} H_i S_j - \lambda^2 \Lambda_{ij} S_i S_j + A_{ij}(\text{Cu}) S_i I_j + A'_{ij}(\text{N}) S_i I'_j] \quad \dots (6)$$

the terms having their usual significance. Remembering that the ion in question is situated in a field of D_{4h} symmetry,

$$H_S = \beta [g H_{\parallel z} S_z + g_{\perp} (H_x S_x + H_y S_y)] + \lambda^2 (\Lambda_{\perp} + \Lambda_{\parallel}) S_z^2 - \lambda^3 \Lambda_{\perp} S(S+1) + A_{\parallel} S_z I_z + \frac{1}{2} A_{\perp} (S_+ I_- + S_- I_+) + A' S_z I'_z \quad \dots (7)$$

In the above expression, the primed terms refer to the nitrogen nuclei. A' has been assumed isotropic, basing on the experimental observation.

Referring (7) to laboratory coordinates, and eliminating those terms whose time average is zero and also those which produce equal shifts to all the levels, we get

$$H_S = g\beta H S_z + D S_z^2 + A_{\parallel} S_z I_z + \frac{1}{2} A_{\perp} (S_+ I_- - S_- I_+) + A' S_z I'_z \quad \dots (8)$$

where $g = \frac{1}{2}(g_{\parallel} + 2g_{\perp})$ and $D = \lambda^2(\Lambda_{\perp} - \Lambda_{\parallel})$

Now $g_{\parallel} = 2.0023(1 - \lambda \Lambda_{\parallel})$

and $g_{\perp} = 2.0023(1 - \lambda \Lambda_{\perp})$

$$\text{where } \Lambda_{\parallel} = \sum_{n \neq 0} \frac{\langle 0 | L_z | n \rangle \langle n | L_z | 0 \rangle}{E_n - E_0}$$

$$\Lambda_{\perp} = \frac{1}{4} \sum_{n \neq 0} \frac{\langle 0 | L_+ + L_- | n \rangle \langle n | L_+ + L_- | 0 \rangle}{E_n - E_0}$$

$|0\rangle$ being the ground state orbital wave function and the $|n\rangle$ representing the excited states. Using the wave functions in (1), we get

$$g_{\parallel} = 2.0023 \left[1 - \frac{4\lambda a_1^2 a_4^2 \left\{ 1 + \left(\frac{b_1 + b_4}{a_1 + 2a_4} \right) S \right\}^2}{E(B_{2g}) - E(B_{1g})} \right]$$

$$g_{\perp} = 2.0023 \left[1 - \left\{ \frac{\lambda a_1 a_3 b_1 b_3 \left(\frac{a_1 a_3}{b_1 b_3} + \frac{b_1 b_3}{a_1 a_3} - \sqrt{2} \right)}{E(E_g) - E(B_{1g})} + \frac{S\lambda(\sqrt{6}a_3 b_1 - a_1 b_3)(2a_1 a_3 - \sqrt{2}b_1 b_3)}{E(E_g) - E(B_{1g})} \right\} \right] \quad \dots (9)$$

where S is the overlap between the d and p orbitals, and may be taken as 0.1 approximately^{15,16}.

Substituting the value¹⁷ $\lambda = -829 \text{ cm}^{-1}$ for Cu^{2+} and using the frequencies of the absorption peaks for the purple and red complexes, we obtain

(a) for the purple complex

$$g_{\parallel} = 2.0023 (1 + 0.0960 \xi)$$

$$g_{\perp} = 2.0023 (1 + 0.0262 \zeta) \quad (10a)$$

(b) for the red complex

$$g_{\parallel} = 2.0023 (1 + 0.0858 \xi)$$

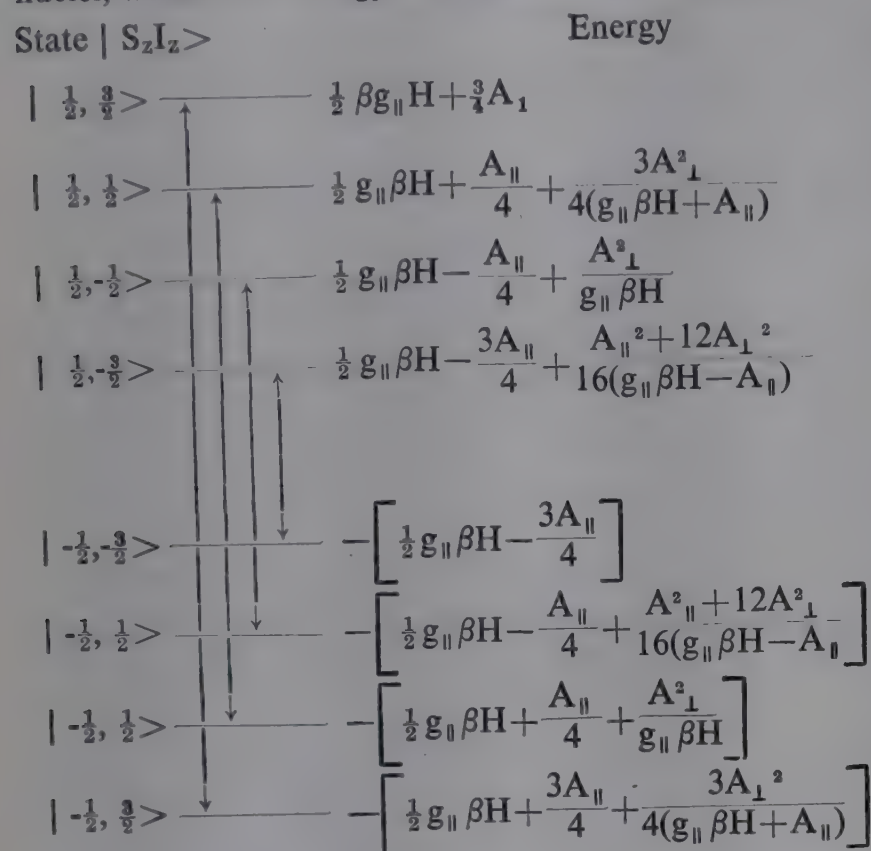
$$g_{\perp} = 2.0023 (1 + 0.0272 \zeta) \quad (10b)$$

$$\text{where } \xi = a_1^2 a_4^2 \left\{ 1 + 0.1 \left(\frac{b_1}{a_1} + \frac{b_4}{2a_4} \right) \right\}^2$$

$$\zeta = a_1 a_3 b_1 b_3 \left[\frac{a_1 a_3}{b_1 b_3} + \frac{b_1 b_3}{2a_1 a_3} - \sqrt{2} \right]$$

$$+ 0.1 (\sqrt{6} a_3 b_1 - a_1 b_3) (2a_1 a_3 - \sqrt{2} b_1 b_3)$$

(B) *Hyperfine Structure*: With the spin-Hamiltonian in (8) and considering the hyperfine interaction with the Cu nuclei, we find the energy level scheme as shown below:



The anomalous line-width of the copper-hyperfine structure has been treated by McConnell¹⁸ and later by Wilson and Kivelson^{19,20} in a greater detail. From our measurements, $A_{\parallel}$ appears to be about 90 oersteds for the red complex and about 95 oersteds for the purple one. But one needs be cautious in drawing further conclusions from there, as the effect of Brownian motion on the line width²¹ has not been considered here. This is further discussed in the concluding section.

The value of $A_{\perp}$ is known^{20,22} to be about one tenth that of $A_{\parallel}$. From the observations on aqueous solutions, it has not been possible to resolve the splittings due to $A_{\perp}$.

(C) *The g-values, and the Degree of Covalency*: Since the solvent, viz., water has got a relatively low viscosity, and also as the copper-hyperfine splittings are large, the centres of the observed ESR spectra of the solutions should correspond to $g_{\parallel}$. Using the experimentally observed $g_{\parallel}$ values and the correlation obtained in the Table 4, the co-efficients a_1 , a_3 and a_4 are calculated, and

substituting these in eqn. (9), $g_{\perp}$ are worked out for the two complexes. The results are collected in Table 5.

TABLE 5

Compound	a_1	a_3	a_4	$g_{\parallel}$	$g_{\perp}$
Purple	0.843	0.853	0.723	2.0902	2.0227
Red	0.883	0.893	0.757	2.0939	2.0285

The degree of covalency, which is expressed by the quantity a_1^2 , is found out to be .711 for the purple complex and .780 for the red one. The value for the purple complex is in fair agreement with that given by Wiersema and Windle²³, who had also studied a copper-biuret complex by ESR, though the colour of the complex was not mentioned by them. Presumably it was the better known purple complex.

(D) *The Pale Green Complex*: The ESR spectrum of the green complex in solution shows no hyperfine splitting due to the ligands, as is to be expected if the bonding is through the oxygens, and only a partially resolved pattern due to interaction with the copper-nucleus. The comparative narrowness of the line indicates that the interaction is somewhat weaker, i.e., the s-character of the orbital is less as compared to the complexes where the bonding is through nitrogens.

(E) *The ESR Spectra of the Solids*: In these the hyperfine splittings are totally suppressed and in the case of the purple and the red complexes, the $g_{\parallel}$ and $g_{\perp}$ lines are only partially resolved. The g-values are determined using the method given by Kneubühl²¹. These are given in Table 6.

TABLE 6

Compound	$g_{\parallel}$	$g_{\perp}$
Purple	2.1635	2.0388
Red	2.1708	2.0463
Pale Green	$g_1 = 2.3583$	$g_2 = 2.0729$ $g_3 = 2.1781$

The values differ from those determined for the solution state, showing the effect of packing and the long range crystal field^{24,27}. But the overall low values and low anisotropies for the purple and red complexes are consistent with their square planar co-ordination. The pale green complex, on the other hand, exhibits g-values typical of octahedral copper-complexes.

Conclusions

The evidence of the ESR spectra, considered together with the symmetry conditions revealed by the optical spectra establishes beyond doubt that in both the purple and the red complexes, the Cu^{2+} ion is co-ordinated in a square planar configuration to four nitrogens belonging to two biuret molecules. The hydroxyl bridge hypothesis of McLellan and Melson thus appears to be open to doubt. The abnormally low magnetic moment reported by them may be ascribed to an incorrect estimate of molecular weight. However, the possibility of dimer formation at the higher pH is quite high for the following reasons:

(a) The line shifts in the optical absorption spectra are too large to be accounted for by the changing dielectric constant of the solvent with changing pH, though the overall character of the spectrum remains the same, showing that the local symmetry at the Cu^{2+} ion sites are unaltered, and a drastic change cannot have taken place.

(b) The absorption line arising from the $B_{1g} \rightarrow B_{2g}$ transition is shifted by the largest extent, and it is precisely these in-plane orbitals which should be most affected by a dimer formation.

(c) The lowering of magnetic moment with temperature observed by Melson in the purple complex does show that there is indeed a super-exchange interaction of anti-ferromagnetic type existing between the cupric ions. The antiferromagnetic exchange will effectively reduce the ligand field, causing a red shift, as observed.

(d) The width of the ESR spectrum of the purple complex is slightly more than that of the red complex. As such, it may not be significant, as many different factors affect the line width. Among these, a faster rotational Brownian motion can reduce the line width, as shown by Kneubühl. On dimer formation, the Brownian angular velocity of the molecule will be reduced due to increased moment of inertia and the increased viscous drag, resulting in a slight broadening of the spectrum as observed. Considered along with the other evidences, this becomes significant.

The rather large difference in the overlap coefficients calculated for the two complexes obviously arises from not taking the copper-copper exchange interaction into account.

From the above, we conclude that the red complex formed at the lower pH dimerises into the purple complex at the higher pH, without undergoing any radical change.

Both of these are converted into identical looking deep blue coloured compounds on exposure to moist air, which gave identical ESR spectra. It lends a further support to the contention presented here.

Acknowledgements

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A quick and accurate method, based upon high frequency titration technique, has been developed for the estimation of SO_4^{2-} in presence of large amounts of Fe^{3+} and Cl^- and has been applied in the estimation of sulphate in CO-conversion catalyst. The method consists of titrating in alcohol-water (40: 60 per cent by vol.) or dioxan-water (40: 60 per cent by vol.) medium against a standard barium acetate solution of the sample after addition of tri-ethanolamine and acetic acid to keep the pH at 4.5-5.5.

High Frequency Titration of Small Amounts of SO_4^{2-} in Presence of Large Amounts of Fe^{3+} and Cl^-

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The application of high frequency titration technique to various analytical problems in fertilizer industry is being studied in this laboratory. It has already been employed in the following estimations:—(i) moisture in various fertilizer ingredients¹⁻⁴, (ii) chloride⁵ in evaporator liquors, and (iii) phosphate, sulphate and fluosilicate in wet process phosphoric acid⁶. This technique has also been applied for quick estimation of free acidity in superphosphates⁷.

It was thought desirable to study the application of this method in the estimation of sulphate content of CO-conversion catalyst samples. In the CO-conversion catalyst⁸, manufactured by this Division of FCI Ltd., by its own process, the sulphate content in the final product has to be kept at a low level (below 1 per cent). A typical catalyst sample contains, on dry basis, Fe_2O_3 78 and Cr_2O_3 6.8 per cent. For quality control, a large number of sulphate estimations have to be carried out on different batches by gravimetric methods, which are time-consuming and not well-suited. A quick and accurate method for estimating sulphate in the catalyst samples by high frequency titrimetry, as developed in this laboratory, is reported in this paper.

Experimental

All the solutions were made in deionized carbon dioxide-free conductivity water and all the chemicals used in these investigations were of A.R. or G.R. quality.

The apparatus used was modified form¹ of that developed by Hall², selected particularly for its simpli-

city of operation and excellent time-stability. It had a conductivity cell with no contact between the plates and solution, thereby removing many errors inherent in the usual conductivity cell.

The circuit (Fig. 1) used for this apparatus was of crystal oscillator-type with some modification³, which has been used for the determination of dielectric constant. An auxiliary vacuum tube voltmeter was required for following the effective overall conductance changes of the cell. The principle of operation is simple.

The instrument has a circuit which gives a direct indication of both effective overall conductance and effective overall capacitance changes of a titration cell, which are read on a calibrated capacitor dial or on a valve voltmeter. A 5U4-GB valve (V_1) provides fullwave rectification from a transformer T through an inductance capacity filter giving a smooth high tension power supply for the oscillator. A regulated H.T. supply for the simple valve voltmeter is obtained across the two neon regulating tubes, V_2 and V_3 . The current carried by V_2 and V_3 is adjusted by means of the variable resistance R_{12} . The resonant circuit of the oscillator valve V_5 (double triode, half of ECC81) comprises the tuning coil L_1 the variable capacitors C_1 and C_2 and the titration cell. Some cells with particular solutions may give a high enough conductance component to dampen the oscillation completely. In such cases the switch and series capacitors— C_3 , C_4 and C_5 —may be used to bring the effective conductance within the range of the instrument. The frequency of oscillation is controlled by a quartz crystal, X, strapped between the

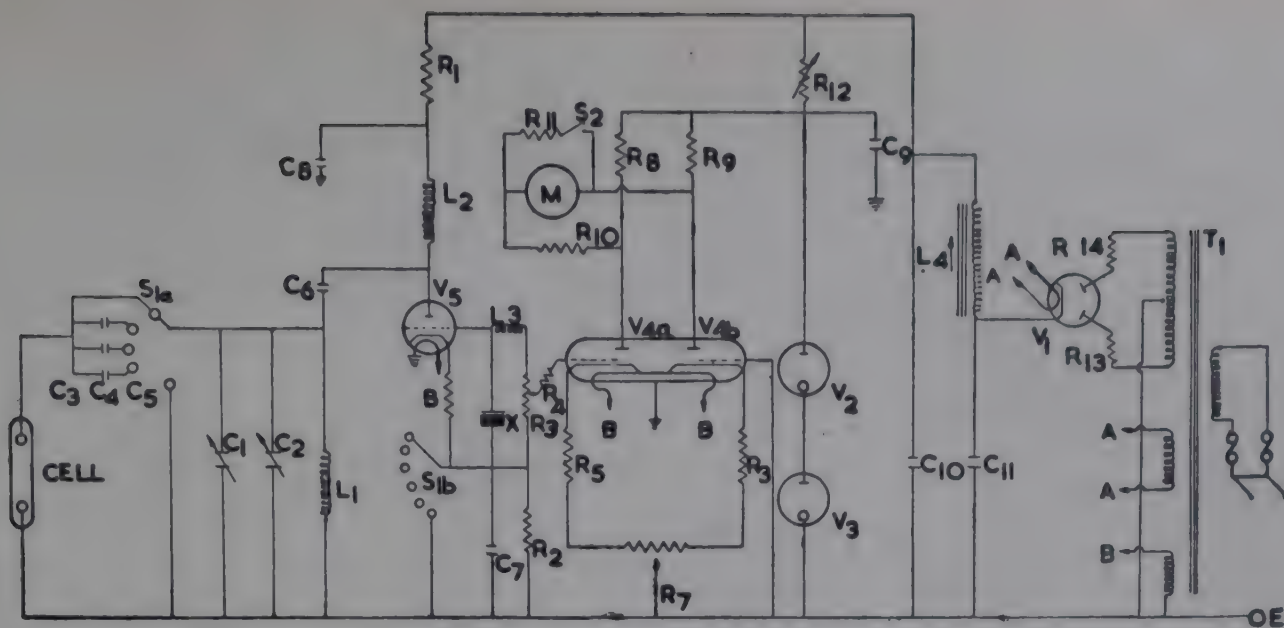


Fig. 1—Circuit of High Frequency Titrimeter

$C_1=100 \mu\mu$ F high stability standard variable condenser (Eddystone, Cat. No. 738) filled with vernier slow-motion dial (Eddystone)
 $C_2=27.5 \mu\mu$ F high stability standard variable condenser (Eddystone Cat. No. 588) fitted with vernier slow-motion dial (Eddystone, Cat. No. 843)
 $C_3=27.5 \mu\mu$ F high stability standard variable condenser (Eddystone, Cat. No. 588) fitted with vernier slow-motion dial (Eddystone, Cat. No. 843)
 $C_4=500 \mu\mu$ F silvermica fixed condenser
 $C_5=200 \mu\mu$ F -do-
 $C_6=100 \mu\mu$ F -do-
 $C_7=100 \mu\mu$ F condenser
 $C_8, C_9=0.10 \mu$ F condenser
 $C_{10}, C_{11}=8 \mu$ F electrolytic condenser, 450-volt D.C. working
 $R_1=33,000$ -ohm resistance
 $R_2=1,500$ -ohm high-stability resistance, 1 per cent tolerance
 $R_3=33,000$ -ohm variable resistance
 $R_4=1$ megohm resistance
 $R_5, R_6=2,200$ ohm high-stability resistance, 1 per cent tolerance

$R_7=1,000$ ohm potentiometer
 $R_8, R_9=30,000$ ohm high-stability resistance, 1 per cent tolerance.
 $R_{10}=820$ ohm -do-
 $R_{11}=47$ ohm -do-
 $R_{12}=20,000$ ohm variable resistance
 $R_{13}, R_{14}=100$ ohm resistance
 L_1 =Turning Coil consisting of 50 turns of 26 gauge enamelled copper wire on a 1-in paxolin former.
 $L_2=2.5$ millihenry radio frequency choke
 $L_3=13$ millihenry frequency choke (Eddystone Cat. No. 1006)
 $V_1=5U_4$ —GB rectifier
 $V_2, V_3=85A_2$ neon regulator
 V_4 =ECC 81
 V_5 =ECC 81 (only one-half used)
 $X=6.2$ megacycles per second crystal, 0.01 per cent (type 10X)
 M =Moving Coil D.C. micrometer 0.250 A with mirror scale

control grid and cathode of the oscillator valve V_5 . The negative bias voltage in the control grid of V_5 is developed across R_3 through the high frequency choke L_3 .

The beaker containing the electrolytic solution was placed in parallel with the capacitor circuit. Different frequencies of 2 to 10 Mc/s can be produced by different piezoelectric quartz crystals. In these investigations a 6.2 Mc/s quartz crystal has been used. The cell was a pyrex glass beaker of 100 ml. capacity with the external electrodes, 3.0 cm. apart, made of copper ribbons (1 mm. thickness, 1.5 cm. breadth). The titrimeter was connected with a voltage stabilizer and the solution to be titrated was stirred by a magnetic stirrer except when the reading was taken. The titrant was added from a 5 ml. microburette having a least count of 0.01 ml. in 0.1 to 0.2 ml. portions. All the titrations were done in very dilute solutions and the total dilution in each case remained the same, i.e. 5 to 10 ml. of stock solution of the sample was diluted to 100 ml.

The effective component method, which is characterized by the fact that every alteration in the composition of the solution produces a change in resonance frequency, was adopted. As a result, the oscillation of the quartz crystal became slow. A change in capacity was necessary to restore the full vibration in the crystal, and due to the change in capacity there was a corresponding change in meter-reading of the instrument which showed the conductance changes of the system. The change in meter-reading following the change in composition of the solution was plotted against the volume (in ml.) of the reagent added.

A weighed amount of catalyst sample (2-3 g.) was taken and dissolved in a minimum amount of hot hydrochloric acid (conc.) in a 400 ml. beaker, and the solution, thus obtained, was cooled and transferred quantitatively to a 250 ml. flask and the volume made up to the mark. From this stock solution, aliquot portions were taken for sulphate ion estimation by the

(i) usual gravimetric method by reduction of ferric to ferrous ions by Devarda's alloy, which was necessary to avoid lower results due to co-precipitation of ferric sulphate with barium sulphate (as ferrous sulphate does not coprecipitate with barium sulphate⁹) and (ii) by the high frequency titration against barium acetate where a non-aqueous medium was used and ferric ion was complexed by an excess of triethanolamine* (about 3 ml. of triethanolamine per 4 mg. of the catalyst samples).

Results and Discussion

The factors which will influence the nature of the high frequency titration curves, besides low frequency curves, are the operating frequency, the dimensions of the cell used and the dielectric constant of the solvent. In the present study, a fixed frequency quartz crystal (6.2 Mc/s) and the same cell of 100 ml. capacity was used in all experiments. Thus, only two major factors, viz., (a) solvent used as medium and (b) concentration of inert electrolytes present in the system, remain, which affect the high frequency titration curves. Barium sulphate is soluble in water to the extent of about 3 mg/l. This solubility is increased by the addition of an acid, but is decreased in the presence of alcohol (1.8 mg./l.) and other non-aqueous solvents. Hence, higher accuracy was possible only when enough non-aqueous solvent was present in the system; in aqueous solutions the determination of milligram quantities of sulphate will not be accurate except by the use of turbidimetry, but this technique could not be applied accurately in present case, as the catalyst forms a coloured solution. Moreover, the titration of very low concentration of sulphate is rapid in non-aqueous solvents indicating that the induction period observed in water for precipitation of small concentration of sulphate is not encountered here. A number of non-aqueous solvents, viz. dioxan, acetone, ethyl and methyl alcohols, have been tried in pure form as well as in mixtures with water in various proportions, and it was found that both 40 per cent absolute alcohol and 40 per cent dioxan gave good results.

The nature of titration curves changes with the nature of concentrations of various foreign ions present in the solution. Hence the effect of foreign ions was studied separately by titrating the sulphate with barium acetate in presence of those ions, which were present in appreciable amounts in the catalyst sample. The main foreign

ions present when the catalyst sample was brought into solution by hydrochloric acid were Fe^{3+} , Cr^{3+} and Cl^- . Studies were first carried out on the determination of a small amount of sulphate present as ammonium sulphate or potassium sulphate along with different concentrations of ferric and chloride ions (Tables 1 & 2). The amount of Cr^{3+} ions in the catalyst solution was comparatively small and did not affect the results of sulphate

TABLE 1—H. F. TITRATION OF K_2SO_4 SOLN. PURE AND IN PRESENCE OF Fe_2O_3 SOLN IN HCl AGAINST 0.02 M $\text{Ba}(\text{CH}_3\text{COO})_2$ SOLN.

Total dilution 100 ml.

No	Vol of K_2SO_4 Soln, ml.	Vol of Fe_2O_3 Soln in HCl, ml.	K_2SO_4 as So_3 , mg		
			Taken	Found	% Error
1.	1.0	*0	1.64	1.63	1.61
2.	2.50	*0	4.10	4.06	0.98
3.	5.0	*0	8.20	8.30	1.21
4.	1.0	5.0	1.64	1.63	0.61
5.	1.0	7.5	1.64	1.62	1.22
6.	1.0	10.0	1.64	1.67	1.83

*Triethanolamine is not added.

TABLE 2—H. F. TITRATION OF $(\text{NH}_4)_2\text{SO}_4$ SOLN. PURE AND IN PRESENCE OF Fe_2O_3 SOLN. IN HCl AGAINST 0.02 M $\text{Ba}(\text{CH}_3\text{COO})_2$ SOLN.

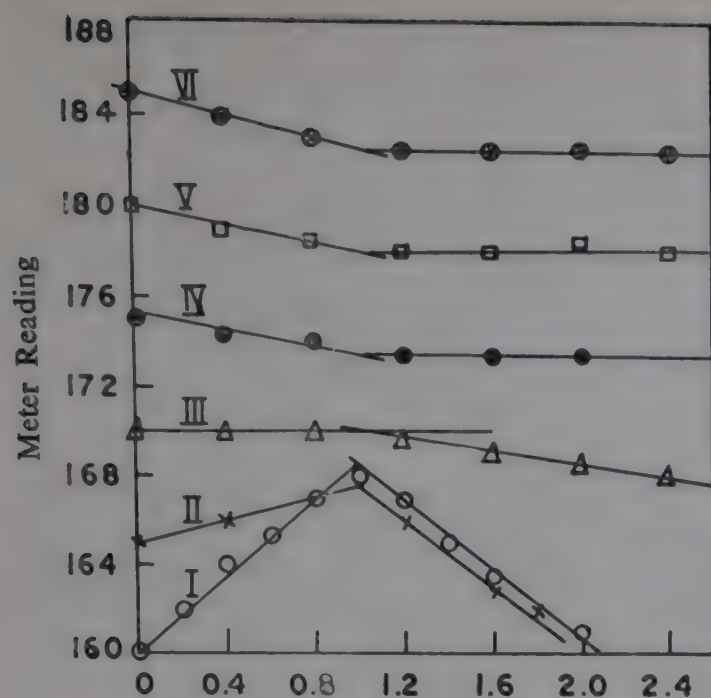
Total dilution 100 ml.

No	Vol of $(\text{NH}_4)_2\text{SO}_4$ Soln, ml.	Vol. of Fe_2O_3 Soln in HCl, ml.	$(\text{NH}_4)_2\text{SO}_4$ as So_3 , mg.		
			Taken	Found	% Error
1.	1.0	*0	0.81	0.80	1.23
2.	2.0	*0	1.62	1.59	1.85
3.	2.5	*0	2.02	1.99	1.48
4.	2.0	1.0	1.62	1.59	1.85
5.	2.0	2.0	1.62	1.60	1.23
6.	2.0	5.0	1.62	1.64	1.23
7.	2.0	10.0	1.62	1.58	2.40
8.	2.0	15.0	1.62	1.66	2.46

*Triethanolamine was not added.

determination in dilute solutions. It was found that in a 40 per cent alcoholic medium pure ammonium sulphate or potassium sulphate gives sharp end-points (Fig. 2); but as the concentrations of Fe^{3+} and Cl^- ions increased, the sharpness and accuracy of end-points gradually

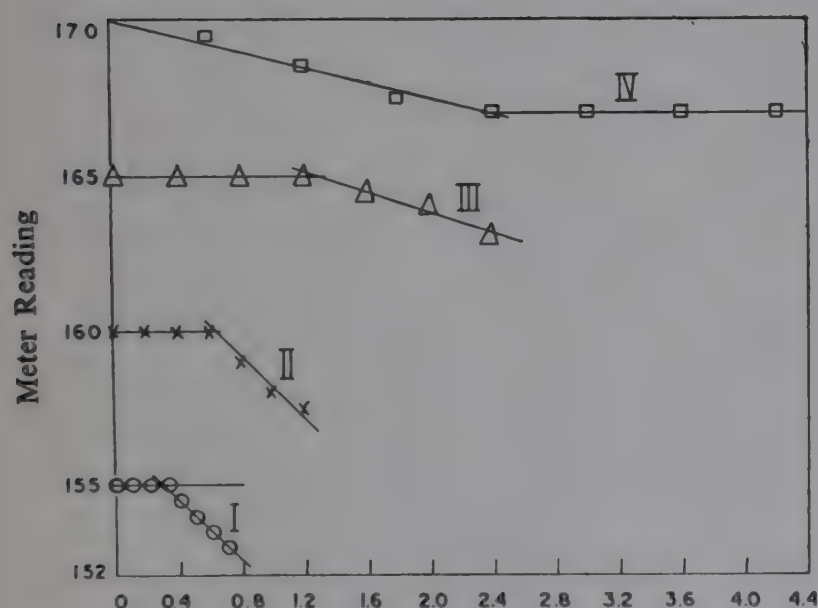
*as triethanolamine does not form a stable complex with barium ions its addition will not affect the results.



Vol. of 0.02M Barium Acetate Soln. Added, ml
Fig. 2—Effect of Fe_2O_3 solution of Ammonium Sulphate
H. F. Titration of Ammonium Sulphate Solution against
0.02M Barium Acetate in Presence of Fe_2O_3 Solution
in HCl

LEGEND

I-2 c.c.	Ammonium Sulphate	Solution (Pure)		
II-2 c.c.	"	"	Solution + 1 c.c. Fe_2O_3 Soln.	
III-2 c.c.	"	"	Solution + 2 c.c. "	"
IV-2 c.c.	"	"	Solution + 5 c.c. "	"
V-2 c.c.	"	"	Solution + 10 c.c. "	"
VI-2 c.c.	"	"	Solution + 15 c.c. "	"



Vol. of 0.02M Barium Acetate Soln. Added, ml.
Fig. 3—H. F. Titration of Catalyst Solution Against 0.02M
Barium Acetate Solution

LEGEND

I-5 cc.	Catalyst	Solution in 40% Alcohol		
II-10 c.c.	"	"	"	"
III-20 c.c.	"	"	"	"
IV-40 c.c.	"	"	"	"

decreased and after a certain stage no break was obtained in the titration curve. The titration curves obtained were of inverted V shape, in pure solutions, giving a very sharp end-point. The shape of the curves depends on the medium of titration and the constant of the instrument used; in the present experiments it was similar to that obtained by Bein¹¹, in titration of sulphate ion. At higher concentrations of ferric oxide, no break was obtained in the curve at all due to increase in the concentration of electrolytes, but this difficulty was overcome when triethanolamine was added in sufficient amounts to complex the Fe^{3+} . The effect of chloride ions was not so prominent at the concentrations in which it is present in the diluted condition of titrating solution.

The following conditions have been found for high frequency titration of small amounts of sulphate in presence of large quantities of Fe^{3+} and Cl^- ions. (1) Titration is to be carried out in a medium of 40 per cent dioxan; 60 per cent water or 40 per cent alcohol; 60 per cent water by volume; (2) Triethanolamine (about 1 ml. per 1 mg. of Fe_2O_3) is to be added to complex Fe^{3+} ; (3) The pH of the solution is to be kept between 4.5 and 5.5 by the addition of acetic acid before titration by dilute solution of barium acetate (0.02M).

Different concentrations of catalyst solutions were titrated under above conditions in 40 per cent alcohol and 40 per cent dioxan. It was found that at higher concentration of catalyst solutions the error increases, while at a lower concentration sharp breaks and accurate end-points are obtained particularly when 5 or 10 ml. of the stock solution was titrated after diluting to 100 ml. (Table 3). The titration curves of different

TABLE 3—H. F. TITRATION OF $(\text{SO}_4)^{2-}$ IONS IN IRON CATALYST
SAMPLE IN DIFFERENT CONCENTRATIONS AGAINST 0.02 M
 $\text{Ba}(\text{CH}_3\text{COO})_2$ SOLN.

Total dilution 100 ml.

Solvents	No	Vol of the soln. ml.	Wt % of SO_3 in the sample.		
			By stdz. method	By H.F. method	% Error
40% dioxan	1	5.0	0.41	0.41	2.43
	2	10.0	0.41	0.42	2.38
	3	20.0	0.41	0.40	2.43
	4	40.0	0.41	0.43	3.02
40 absolute alcohol.	1	5.0	1.05	1.04	0.95
	2	10.0	1.05	1.03	1.90
	3	20.0	1.05	1.02	2.85
	4	40.0	1.05	1.02	2.85

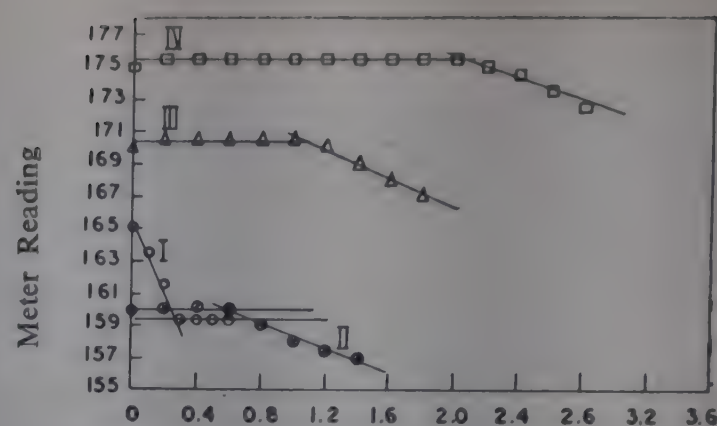
TABLE IV—H. F. TITRATION OF $\text{SO}_4^{=}$ IONS IN IRON CATALYST SAMPLE AGAINST 0.02 M $\text{Ba}(\text{CH}_3\text{COO})_2$ SOLN.

Total delution 100 ml.

Sample No.	Wt % of SO_3 in the sample.		
	By stdz. method	By H. F. method.	
		In 40% alcohol	
		Found	% Error
1	0.52	0.51	1.92
2	1.34	1.32	1.49
3	1.04	1.06	1.92
4	0.44	0.45	2.27
5	0.50	0.51	2.00
6	0.52	0.51	1.92
7	0.50	0.49	2.00
8	0.41	0.40	2.44
9	0.48	0.47	2.08

concentrations of the same catalyst in presence of 40 per cent alcohol and 40 per cent dioxan are given (Figs. 3 & 4), Fe^{3+} ions being masked by triethanolamine.

The determination of sulphate content in different catalyst samples obtained from the catalyst plant were carried out by high frequency titration technique under above conditions. The results obtained by high frequency titration are comparable with those obtained by usual gravimetric procedure used and the error does not exceed 3 per cent (Table 4).



Vol. of 0.02M Barium Acetate Solution Added, ml
Fig. 4—H. F. Titration of Catalyst Solution Against 0.02M Barium Acetate Solution

LEGEND

I-	5 c.c. Catalyst Solution in 40% Dioxan
II-	10 c.c. " " " "
III-	20 c.c. " " " "
IV-	40 c.c. " " " "

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Gas chromatograms at single column temperatures fail to reveal peaks and shoulders for all the components in a complex sample. For the unambiguous identification of the multi-component peaks, it has been suggested to run isothermal chromatograms at three or more temperatures and then apply various characteristics of the phenomenon of retention index-column temperature. A greater accuracy in the experimental retention index, coupled with use of subtractive, selective and superior columns, can vastly improve the characterization power of gas chromatography.

Maximum emphasis has been given on the linearity of the retention index of hydrocarbon peaks with column temperature for qualitative analysis (upto C_9 hydrocarbons) of different Indian naphthas, viz. those from Barauni, ESSO, Burmah Shell, Gujarat and Indian Oil Corporation (Assam Crude). Quantitative analysis of the major components in a few naphtha samples has also been included.

Application of Temperature Coefficient of Retention Index in the Gas Chromatographic Analysis of Naphtha

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A rapidly growing importance of naphtha as a feed-stock for various industries has created a great demand on its detailed composition by speedy and reliable methods. Since the last decade, gas chromatography has been used extensively for the analysis of hydrocarbon samples¹⁻⁹. It is agreed that the ideal chromatogram where a peak represents no more than a single hydrocarbon is impossible for complex products like naphtha and gasoline. Naturally, one has to reconcile with the presence of many doublets, triplets and multiplets in an isothermal or programmed temperature chromatogram.

The object of the present study is to suggest new parameters for the unambiguous identification of multi-component peaks. The phenomenon of retention index-column temperature has a great potential in this regard. Ettre and Billeb¹⁰ initiated work on the relationship of retention index with column temperature in GLC. This work was followed by several workers, including Widmer,¹¹ Hiveley and Henton¹² and Matukuma¹³. Saha and Mitra¹⁴ pointed out that the linearity of retention index with temperature is a versatile phenomenon, independent of types of solutes and partitioning liquids. Hence the properties associated with I-T phenomenon can be successfully utilized as new parameters for the identification of peaks and shoulders from gas chromatograms.

Therefore, by running a complex chromatogram at three or more temperatures and by observing the shift in retention index, appearance and disappearance of peaks and shoulders, coelution and peak inversion, it is quite possible to confirm the identity of individual hydrocarbons. In this perspective the potentialities and effectiveness of improved and selective columns can be better exploited. In a very few cases, where multiplets cannot be satisfactorily resolved by the principle of temperature coefficient alone, reaction gas chromatography¹⁵⁻²¹ may be employed.

Another aim of this work is to demonstrate the application of the above concepts for rapidly determining the composition of Indian naphthas—obtained from different crudes and refineries—particularly with respect to their major components. Virtual non-existence of published information²² on the composition of Indian naphthas definitely adds to the value of this investigation.*

Experimental

A 13' $\times$ 1/8" O.D. copper tube packed with 60/80 mesh (B.S.S.) Gas Chrom Q, containing approximately

* Abbreviations used for the hydrocarbons in this paper are the same as used by the present authors in their earlier work^{14,23}.

5 per cent squalane was the only column used in this investigation. The gas chromatograph was an Aero-graph 550 equipped with a flame ionization detector, coupled to a Honeywell recorder with a disc area integrator. The gas hold-up was taken as usual from methane retention time.

A subtraction column of 6" $\times$ 1/8" O.D. glass tube, containing specially prepared mercury perchlorate on 60/80 mesh Chromosorb P, was used for preferential elimination of all unsaturated hydrocarbons—acetylenic, olefinic and aromatic.

Results

Chromatograms at multiple column temperatures readily provide details of the phenomenon of I-T relations, like the change in resolution of adjacent peaks, appearance and disappearance of shoulders and crossing of peaks, etc. These informations cannot be obtained from a chromatogram at any single column temperature. However, by chromatographing at three temperatures, it was possible to identify the peaks (vide Tables 1 and 2) in an ASTM** and an aliphatic** naphtha. Similar peak identification is given in Table 3 for an ESSO hexane naphtha.

It has been found that ESSO naphtha contains many hydrocarbons with more than eight carbon atoms; but the identification of peaks in this work was confined upto the retention index of 800 only. Barauni naphtha was run at two column temperatures, viz. 55° and 80°C. (vide Table 4), although a single chromatogram is shown

TABLE 1—IDENTIFICATION OF PEAKS IN A.S.T.M. NAPHTHA

Peak Number	Retention Indices at			Compound
	55°C	80°C	100°C	
1.	586	587	586	3 MP
2.	600	600	600	nH
3.	630	633	636	MCP
4.	666	668	669	2 MH
5.	676	678	679	3 MH
6.	688	690	692	3 EP
7.	700	700	700	nHp
8.	728	731	736	MCH, 2233 TMB
9.	734	—	—	24 DMH
10.	745	748	756	Tol.
11.	764	765	766	2 MHP
12.	772	772	774	3 MHP
13.	785	790	793	IT ₄ DMCH, IC ₃ DMCH

Tol is the symbol for toluene

** Both purchased from Phillips Petroleum Co. of USA.

TABLE 2—IDENTIFICATION OF PEAKS IN ALIPHATIC NAPHTHA

Peak Number	Retention Indices at			Compounds
	55°C	80°C	100°C	
1.	700	700	700	nHp
2.	728	730	731	25 DMH
3.	734	—	—	24 DMH
4.	748	750	756	Tol.
5.	764	764	765	2 MHP
6.	772	773	773	3 MHP
7.	785	790	795	IT ₄ DMCH, IC ₃ DMCH
8.	800	800	800	nO

TABLE 3—IDENTIFICATION OF PEAKS IN ESSO NAPHTHA

Peak Number	Retention Indices at				Compounds
	55°C	80°C	100°C	115°C	
1.	400	400	400	—	nB
2.	473	476	476	—	2MB
3.	500	500	500	500	nP
4.	536	540	543	546	22DMB
5.	571	571	571	572	2 MP
6.	586	585	586	—	3 MP
7.	600	600	600	600	nH
8.	630	632	636	640	MCP
9.	641	648	651	655	B _z
10.	667	668	—	—	2MH
11.	677	677	677	678	3MH
12.	690	692	—	—	224TMP
13.	700	700	700	700	nHp
14.	727	732	738	741	MCH, 2233TMB
15.	732	737	746	—	24 DMH
16.	747	750	758	—	Tol.
17.	765	764	766	764	2 MHP
18.	773	772	774	774	3 MHP
19.	786	790	794	—	IT ₄ DMCH, IC ₃ DMCH
20.	800	800	800	800	nO

Bz is the symbol for benzene.

in Fig. 1(B). Four more naphthas, viz. Burmah Shell's, IOC's, Gujarat gasoline and ASTM Precipitation, were run at a single column temperature (Fig. 2) in order to demonstrate their variations in composition. The identification of peaks in these naphthas (Table 5) is obviously tentative e.g., compounds differing by say ± 2 index units from the observed retention index of a peak cannot be excluded from the information obtained from a single chromatogram. For the final confirmation of olefinic and aromatic hydrocarbons, Barauni and other naphthas (Table 6) were run with and without a mercury perchlorate post-column subtraction under identical operating conditions. As an illustration, subtraction

TABLE 4—IDENTIFICATION OF PEAKS IN BARAUNI NAPHTHA

Peak Number	Retention Indices at		Compound
	55°C	80°C	
1.	400	400	nB
2.	473	474	2MB
3.	500	500	nP
4.	536	540	22 DMB
5.	571	570	2 MP
6.	585	585	3 MP
7.	600	600	nH
8.	628	632	MCP
9.	641	647	B _z
10.	666	668	2MH
11.	676	676	3 MH
12.	690	692	224 TMP
13.	700	700	nHp
14.	728	731	MCH, 2233 TMB
15.	747	750	Tol.
16.	764	765	2 MHP
17.	772	773	3 MHP
18.	786	790	IT ₄ DMCH, IC ₃ DMCH
19.	800	800	nO

chromatograms are shown [Fig. 1(A)] for the Barauni naphtha only.

For quantitative GC work, peak areas were determined from traces of disc chart integrator. The results of calibration with synthetic mixtures are given in Table 7. The use of a single attenuation, peak heights limited to 20 to 80 per cent of the recorder scale, optimized detector sensitivity with a stable base-line and a small sample size was found to give better quantitative results. The quantitative composition of ESSO naphtha and of the two American naphthas, are given in Table 7.

Discussion

Hupe's graphical method²⁴ of computing retention index was slightly modified in this study by plotting the retention distance (on a semi-log paper after correction for gas hold-up) against carbon number in a single line, the spacings between two adjacent normal paraffins being divided into 100 equal units. This has eliminated the necessity for actually chromatographing all the normal paraffins concerned, because the plot of log retention against carbon number has been found to be strictly linear for all normal paraffins.

In the identification of peaks and shoulders in all the chromatograms presented, maximum emphasis was given to the characteristics of the elution behaviour of hydrocarbons with the change in column temperature.

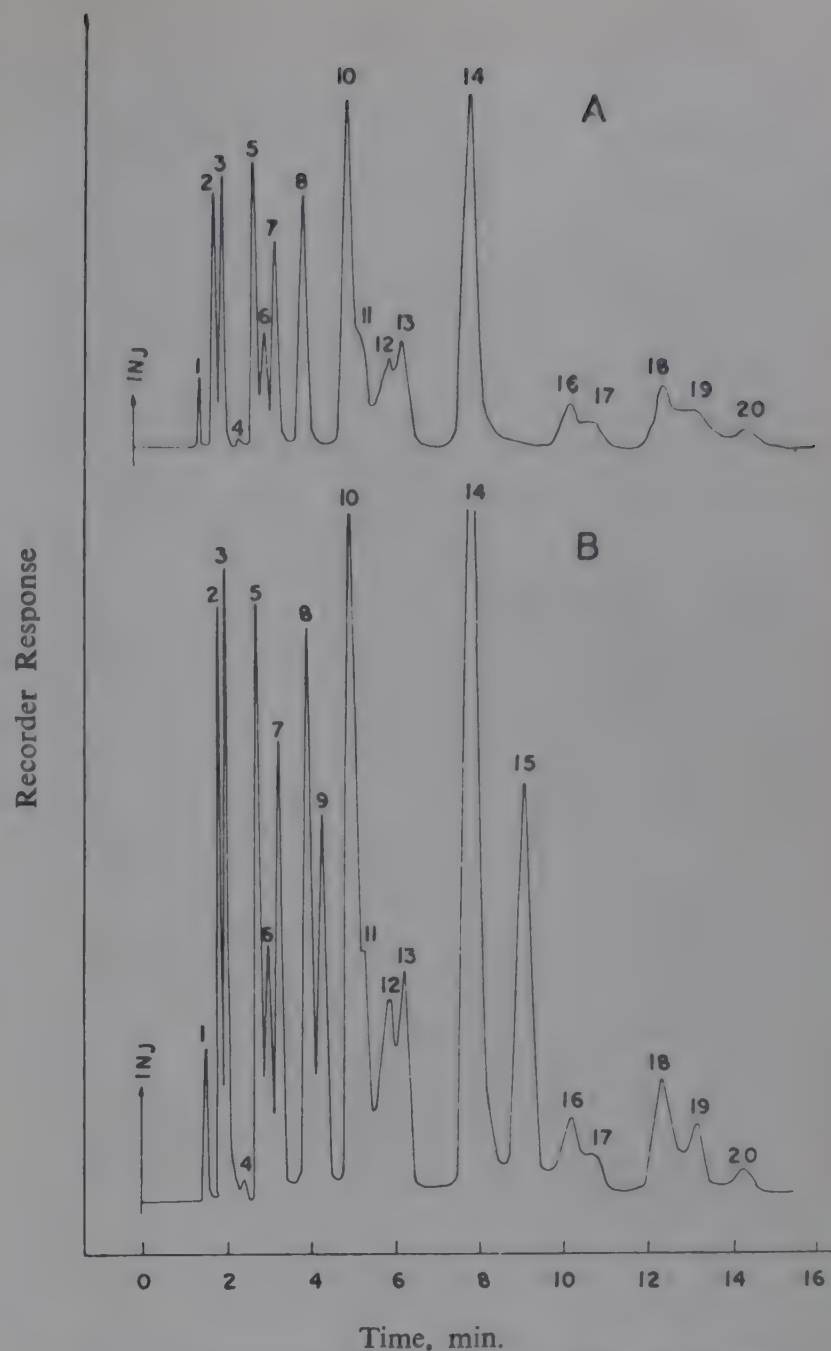


Fig. 1—Chromatograms of Barauni Naphtha at 80°C

A—With Subtraction

B—Without Subtraction

It has been established¹⁴ that (i) retention indices of iso-paraffins and naphthenes increase linearly with column temperature, (ii) the olefins and aromatics usually present in naphthas also give linear I-T plots in non-polar stationary liquids like squalane, (iii) the temperature coefficient of retention index is very characteristic of the type and degree of branching of hydrocarbons (iv) the phenomena of coelution, peak inversion and peak shift with column temperature provide valuable information in deciding the absence or presence of a compound in a peak. Due considerations were given to these findings in confirming the identity of peaks and shoulders in the identification tables.

As an illustration, let us consider peak number 8 in Table 3. The index value of 630 at 55°C in squalane will

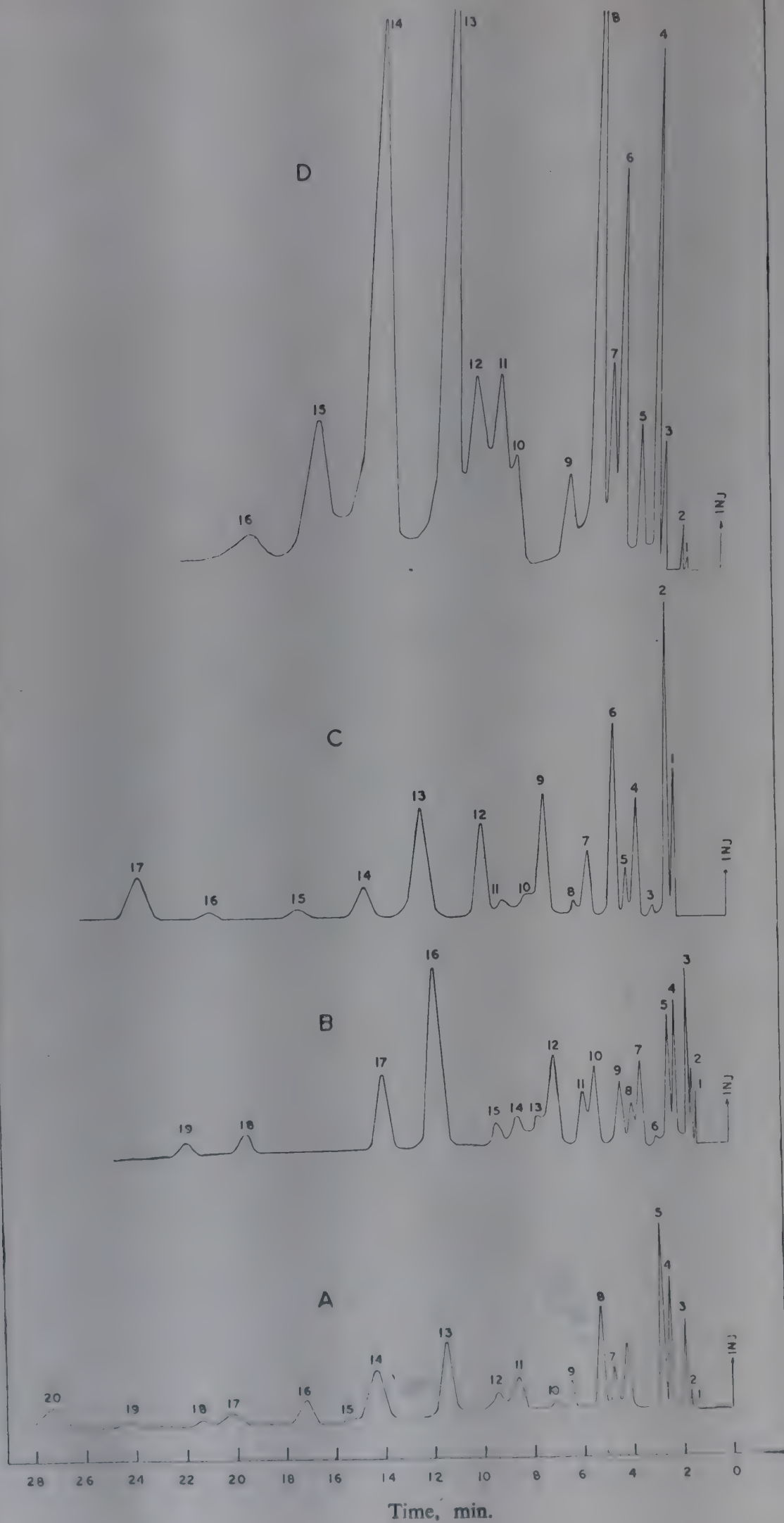


Fig. 2—Chromatograms of
of Naphthas at 55°C

A—Burmah Shell Gasoline
B—Indian oil (Assam) Gasoline
C—Gujarat Gasoline
D—ASTM Precipitation Naphtha

TABLE 5—TENTATIVE IDENTIFICATION OF PEAKS IN DIFFERENT NAPHTHAS BASED ON CHROMATOGRAM AT A SINGLE TEMPERATURE (55°C) FROM A 13' × 1/8" SQUALANE COLUMN

Peak No.	Burmah Shell		Gujarat Gasoline		Indian Oil Corpr.		Precipitation Naphtha A.S.T.M.	
	55° Isq	Compound	55° Isq	Compound	55° Isq	Compound	55° Isq	Compound
1	2	3	4	5	6	7	8	9
1.	371	2M Pr.	472	2MB	300	n-Pr.	300	n-Pr.
2.	400	nB	500	nP	370	2M Pr.	370	2M Pr.
3.	473	2MB	537	22DMB	400	nB	472	2MB
4.	500	nP	569	CP, 2MP, 23 DMB	473	2MB	500	nP
5.	537	22DMB	585	3MP	500	nP	536	22DMB
6.	570	CP, 2MP, 23 DMB	600	nH	536	22DMB	570	2MP, CP, 23 DMB
7.	586	3MP	631	MCP, 24DMP	570	2MB, CP, 23 DMB	584	3MP
8.	600	nH	642	B _z , 223TMB	584	3MP	600	nH
9.	630	MCP, 24 DMP	665	2MH, CH,	600	nH	628	MCP, 22DMP
10.	642	B _z , 223TMB	677	3MH	628	MCP, 22DMP	666	CH, 2MH
11.	666	2MH, CH	690	224TMP	640	B _z , 223 TMB	675	3MH
12.	677	3MH	700	nHp	666	2MH, CH	700	nHp
13.	700	nHp	728	25DMH, MCH, 2233 TMB	676	3MH	726	MCH, 2233TMB
14.	728	25 DMH, MCH, 2233TMB	748	Tol	688	3EP	744	33 DMH
15.	734	24 DMH	766	2MHp, 4MHp	700	nHp	763	2M3EP, 23 DMH 2MHp, 233TMP
16.	748	Tol.	787	IT ₄ DMCH, IC ₃ DMCH, 11 DMCH	728	25DMH, MCH, 2233TMB	771	3MHp, 34DMH, 3EH
17.	765	2MHp	800	nO	748	Tol		
18.	773	3MHp, 3M3EP			787	IT ₄ DMCH, IC ₃ DMCH, 11 DMCH		
19.	787	11 DMCH, IC ₃ DMCH, IT ₄ DMCH			800	nO		
20.	800	nO						

Pr is the symbol for propane

TABLE 6—COMPARISON OF COMPOSITION OF MAJOR PEAKS IN DIFFERENT NAPHTHAS

Compound	% Present in		
	Alphatic	ASTM	ESSO
nB	—	—	0.9
2MB	—	—	3.1
nP, 22DMB	—	—	7.4
2MP	—	—	4.7
3MP, nH	—	11.4	14.3
MCP,	—	1.2	—
MCP, B _z	—	—	3.8
2MH, 3MH	—	11.7	11.4
3EP	—	9.0	—
224 TMP, nHp	—	—	14.4
nHp	15.0	27.8	—
MCH, 2233TMB, 24 DMH	—	30.2	8.6
24DMH, 25 DMH	53.0	—	—
Tol	23.4	6.9	3.9
2MHp, 3MHp	5.6	2.6	8.6
IT ₄ DMCH, IC ₃ DMCH, nO	0.9	1.2	13.3
Higher hydrocarbons (I>800)	—	—	5.0

include both 2, 4-dimethyl-pentane and methylcyclopentane (olefins were not considered). But the retention indices at three more temperatures, their linearity and temperature coefficient unmistakably exclude the possibility of 2, 4-dimethylpentane. The usefulness of the various I-T correlations in clear-cut resolution of multiplets in complex chromatograms can also be seen from the comparison of results in Tables 3 and 5. The retention indices of hydrocarbons reported by Matukuma¹³, Evans²⁵ et al. and others^{26, 27} were very helpful in this work. Table 5 has resulted from consideration of a single isothermal chromatogram and the peaks necessarily contain many doublets and multiplets. Being derived from chromatograms at four temperatures, Table 3 contains single saturated hydrocarbon in each peak except those of 14 and 19. Both methylcyclohexane and 2, 2, 3, 3—tetramethylbutane (in peak 14, Table 3) have the same or very close retention index²⁵ in the range of 25° to 100°C in squalane. This and other similar cases involving isoparaffins and cycloparaffins can, however, be resolved by using highly²⁸ specific columns or a

TABLE 7—CALIBRATION WITH SYNTHETIC MIXTURE

(a) With Constant Attenuation

Compound	Counts	% Found	% Present	% Error	Attn.
23 DMB	75	12.9	12.21	+5.6	× 8
3 MP	95	15.9	15.55	+2.0	× 8
3 MH	192	23.7	23.99	-1.3	× 8
nHp	283	47.4	47.45	-0.1	× 8
Total	645	99.9	99.20		

(b) With Variable Attenuation

Compound	Attenuation	Attn. Factor	Counts × Attn. Factor	% Found	% Present	% Error
23 DMB	× 16	1	517	10.0	12.21	-17.6
3MP	× 16	1	750	14.7	15.55	- 5.0
3MH	× 32	2	660 × 2	25.8	23.99	+ 7.2
nHp	× 32	2	1260 × 2	49.4	47.45	+ 4.0
Total	—	—	4807	100.1	99.2	

micro-hydrogenator post-column. For example, the retention indices of 2,4-dimethylpentane and methylcyclopentane are 623 and 651 respectively at 55°C in polypropylene glycol²⁹ (both the compounds have about the same value in squalane at 55°C). This implies that multiplets in squalane phase involving iso- and cycloparaffins can be resolved by using a polypropylene glycol column.

The effectiveness of the principle of temperature coefficient of retention index in peak identification can be vastly improved by increasing the accuracy and reliability of index value from the present limit of 1 to 0.1 unit, coupled, of course, with columns of superior separation efficiency. Considerable improvement of commercial equipments to permit much more stringent control of temperature, pressure, flow profile and other disturbing factors is needed to achieve this accuracy in retention index. In addition, a few normal paraffins, if not already present, will have to be injected along with the sample for accurate calculation of retention index. Since benzene and toluene emerged as separate peaks from squalane, their detection from the subtraction chromatogram was very easy. However, the olefins were found to hide in some of the major saturated hydrocarbon peaks from squalane column and hence their confirmation by the subtraction technique posed a problem. Decrease in peak areas or peak heights compared against one or more marker peaks (which are free from unsaturates) is a clear indication of the presence of olefins. Thus, peak numbers 1,2,7 and 14 in ESSO naphtha and 2,3 and 14 in Barauni naphtha were suspected to contain olefins. For sure identification of olefins, the separating

column^{30,31} should be so chosen as to reveal the individual olefinic shoulders in the multi-temperature chromatograms by virtue of their differential I-T behaviour from saturated hydrocarbons. The subsequent subtraction pattern will then give correct assignment of peaks to individual olefinic hydrocarbons.

Since quantitative injections by commercial micro-syringes are not always reliable, the summated peak area was taken as proportional to the amount of sample. It is known³² that no significant deviation is obtained in the response factors of different hydrocarbons from a flame ionization detector. The method was standardized with pure reference hydrocarbons as well as with calibrated mixtures†. The results are accurate within ± 4 per cent by weight. It was observed (Table 7) that the change of attenuation and the response of peaks going out of scale did not give proportional change in the counts from area-trace.

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† Purchased from the Polyscience Corpr. of USA.

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Explosion temperatures, (E_T) have been determined with only small amount of ammonium nitrate by gradually heating the sample sealed in pyrex glass tubes. The effect of some of the sensitizers and desensitizers on E_T have been studied. With the increase in the confinement volume E_T of pure ammonium nitrate increases. In the presence of some of the sensitizers E_T remains unchanged with increase in the confinement volume. Whereas when the sample contained some of the known desensitizers E_T was lowered with increase on the confinement volume. The results are discussed.

Explosivity of Ammonium Nitrate

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Over thirty-five fire or explosions of varying intensity involving fertilizer grade ammonium nitrate have so far been recorded. Loss of lives and property in some of these explosions were heavy. Most damaging were the explosions that occurred at the Texas City docks, U.S.A. in the holds of two ships where more than 500 lives were lost and loss of property was estimated to be more than 100 million dollars. Hazards associated with the manufacture, handling and storage of ammonium nitrate have long been recognised and many countries prefer to

produce only the diluted product like calcium ammonium nitrate, nitro-limestone, nitro-chalk, nitro-shell with varying nitrogen content. Since the dilution of ammonium nitrate increases considerably cost of production, packaging, freight and distribution of the fertilizer, the necessity as well as the extent of dilution needs constant reappraisal in the light of recent researches in the field of the explosivity of ammonium nitrate.

Pure ammonium nitrate is quite stable at ordinary

temperatures. When heated it melts at 169°C and soon after dissociates into ammonia and nitric acid and starts evolving nitrous oxide and water. It has been shown that ammonium nitrate without confinement does not explode even when heated to 410°C. Many workers²⁻⁵ have reported that ammonia inhibits decomposition reaction completely even at elevated temperatures. Substances such as calcium carbonate, urea and zinc oxide have been found to inhibit the decomposition of ammonium nitrate and thus stabilize it⁶⁻⁸. One common feature of all the above inhibitors is that they liberate ammonia at elevated temperatures.

It was found that the rate of decomposition and acidity of the melt were closely related^{3,9}. Madany and Burnett¹⁰ showed that decomposition of ammonium nitrate was inhibited by the addition of buffers used to control the acidity of the melt. It was shown in this laboratory that gases evolved during the decomposition of ammonium nitrate on being heated abruptly from alkalinity to acidity at a definite temperature with a given rate of heating. The addition of calcium carbonate, urea and zinc oxide increased this transition temperature to a varying extent.

For explosive decomposition of pure ammonium nitrate by thermal means it is necessary to have the existence of confinement which allows the product gases to develop a pressure of 100 kg./sq. cm. and the temperature around 300°C^{1,6}. The above limiting conditions are brought down considerably in the presence of many impurities. The minimum explosion temperature of ammonium nitrate contaminated with some of the substances are¹: decayed wood 125°C; sugar 170°C; saw dust, 220°C; paper 230°C, jute fibres 250°C.

The crucial role played by the pressure exerted by the product gases due to confinement during explosive decomposition of the salt is not completely understood. Various explanations have however, been advanced. Torsuev¹² thought that the explosion resulted from the explosive decomposition of nitrous oxide in the gas phase. Kaiser¹³ showed that exothermic reactions could occur in the gas phase above the heated salt. According to Feik and Hainer¹⁴ confinement repressed highly endothermic dissociation of the salt and thereby making the decomposition process self accelerating one. Endothermic dissociation of ammonium nitrate has not been considered as a barrier to the spontaneous decomposition of the salt by Rozman¹⁵ who maintained that explosive decomposition could still occur on account of auto catalysis by nitrogen dioxide and water produced as a result of thermal decomposition of ammonium nitrate. It has also been suggested that under confine-

ment the normal decomposition reactions producing ammonia, nitrous oxide and water give way to highly exothermic reactions causing explosive decomposition of the salt^{16,17}.

In the present work explosivity of ammonium nitrate has been studied with particular reference to the influence of confinement.

Experimental

Explosion were carried out in an iron block (diam. 15 cm, height 20 cm.) with three vertical holes, (each 10 cm. deep) one for the thermometer and the other two for samples. The block was mounted on an iron stand. Rise in temperature in all three holes were found to be identical. The block was completely enveloped by a galvanised iron sheet provided with a hole at the top for thermometer. A transparent perspex sheet was placed in front to read the explosion temperature safely. The block could be heated to a maximum rate of 5°C/min.

A small amount of the sample (0.5 g.) was sealed in pyrex tube with dia. 1 cm. and wall thickness, 0.9 mm. Confinement volume was varied by taking varying length of pyrex tube. The block was then heated to 150°C and the two sealed tubes containing the samples were dropped gently in the two holes. The temperature of the block was raised at a constant rate of 2°C/min. Explosions with loud report occurred almost simultaneously and both glass tubes containing the samples were reduced to fine powder. The temperature was immediately recorded.

Discussion

It is important to note that the explosion temperature is the last temperature recorded to which the samples were heated at the moment of explosion when the sudden increase in pressure caused complete disintegration of the glass tubes. The actual temperature of the sample, however, is likely to be higher because of the exothermicity of decomposition reactions under confined conditions. The amount of sample being small the explosion temperature recorded may not be the true explosion temperature of ammonium nitrate but the E_T values of the samples of ammonium nitrate with or without additives generally follow the expected pattern. This method, therefore, affords a safe and reliable means of determining the hazardous nature of ammonium nitrate containing fertilizers.

Pure ammonium nitrate as well as the sample containing by its weight of sensitizers such as sodium chloride, paraffin wax or paper did not explode when

TABLE 1—EFFECT OF ADDITIVES (2%) ON EXPLOSION TEMPERATURE OF AMMONIUM NITRATE (0.5 g.)
(Heating rate—2°C/min.)

Samples	Explosion Temperature at Confinement Volume 3ml., °C	Explosion Temperature at Confinement Volume 6ml., °C	Samples	Explosion Temperature at Confinement Volume 3ml., °C
NH ₄ NO ₃	285	—	NH ₄ NO ₃ +2% urea	333
„ +2% NaCl	213	213	„ +2% CaCO ₃	312
„ +2% NH ₄ Cl	214	215	„ +2% ZnO	340
„ +2% Paper	220	220	„ +2% K I	286
„ +2% Jute	250	250	„ +2% Gypsum	287
„ +2% paraffin wax	223	—	„ +2% Clay	286
			„ +2% CaHPO ₄	287

heated gradually in fully vented system. In some of the experiments, a piece of filter paper dropped in the heated sample of ammonium nitrate in which wax was present caught fire and burnt. When the sample of ammonium nitrate (0.5 g.) sealed in pyrex tubes with confinement volume of 3 ml. was gradually heated at the rate of 2°C/min. it exploded at 285°C. Addition of urea, zinc oxide and calcium carbonate to the extent of 2 per cent by weight of ammonium nitrate increased the explosion temperatures to 333, 340 and 312° respectively as shown in the Table 1. This confirms the findings of Braconier and Delsemme⁶ who found that all substances liberating or aiding the liberation of ammonia stabilized ammonium nitrate and increased its explosion temperature. Herquet¹, however, failed to notice any stabilizing influence of urea on explosion characteristics of ammonium nitrate.

The effect of various sensitizers on the explosion temperature shows that sodium and ammonium chlorides decrease the explosion temperature significantly from 285 to 214°C. Carbonaceous substances, such as paper, jute and paraffin wax, also lowered the explosion temperature to a great extent as shown in the Table 1. The effect of chloride ion has been attributed to the formation of atomic chlorine and subsequent formation of HCl which by increasing the acidity of melt increased the rate of thermal decomposition of ammonium nitrate. Carbonaceous materials, however, undergo rapid oxidation by ammonium nitrate melt contained free nitric acid present as a result of the dissociation of the salt with considerable release of heat which raises the temperature of the system to a temperature when explosive rate of decomposition is attained.

Contrary to the expectations, substances, such as clay, gypsum, potassium iodide and dicalcium phosphate,

added to the extent 2 per cent by weight failed to have any significant effect on the explosion temperature of ammonium nitrate.

Influence of Confinement

The influence of confinement was studied by taking the same weight of ammonium nitrate i.e. 0.5 g. and varying the confinement volume. The results are given in Table 2 which show that the explosion temperature increased with the increase in the confinement volume. This suggests that the pressure exerted by the product gases is one of the limiting factors for the explosive decomposition of the pure salt. Minimum temperature to which 0.5 g. sample must be heated before it undergoes explosive decomposition is found to be 281°C when the confinement volume was kept at the lowest practicable limit i.e. 2 ml.

The variation in confinement volume, however, was not found to have any effect on samples of ammonium nitrate containing 2 per cent by weight of sensitizers (Table 1). In this case probably the confinement pressure needed for explosion is of small magnitude and is

TABLE 2—EFFECT OF CONFINEMENT (HEATING RATE, 2°C/min.)

Samples (0.5g.)	Confinement Volume, ml.	Explosion Temp, °C
NH ₄ NO ₃	2	281
NH ₄ NO ₃	3	285
NH ₄ NO ₃	4	285
NH ₄ NO ₃	4.5	296
NH ₄ NO ₃	5	304
NH ₄ NO ₃	6	314

attained well before the sample attain the required temperature.

It has been shown that ammonium nitrate sensitized with 1 per cent by its weight of waxes needed confinement pressure of only 3 kg./sq.cm. for its explosion⁶.

When the effect of variation in confinement volume was studied with samples of ammonium nitrate containing 2 per cent by its weight of ammonia liberating substances viz., calcium carbonate, urea or potassium hydroxide unexpected results were obtained. With the increase in the confinement volume the explosion temperature decreased (as shown in Table 3). This decrease in the explosion temperature emphasizes the critical role played by the concentration or partial pressure of

TABLE 3—EFFECT OF CONFINEMENT IN THE PRESENCE OF
DESENSITIZERS (HEATING RATE—2°C/MIN.)

Samples (0.5g.)	Confinement Volume, ml.	Explosion Temp., °C
NH ₄ NO ₃ +2% CaCO ₃	2	326
NH ₄ NO ₃ +2% CaCO ₃	3	310
NH ₄ NO ₃ +2% CaCO ₃	4	307
NH ₄ NO ₃ +2% CaCO ₃	4.5	307
NH ₄ NO ₃ +2% CaCO ₃	5	294
NH ₄ NO ₃ +2% CaCO ₃	6	293
NH ₄ NO ₃ +2% Urea	6	292
NH ₄ NO ₃ +2% KOH	6	291
NH ₄ NO ₃ +2% ZnO	6	340
NH ₄ NO ₃ +2% Urea	3	333
NH ₄ NO ₃ +2% KOH	3	325
NH ₄ NO ₃ +2% ZnO	3	340

ammonia in the product gases during gradual heating of the salt under confinement. Why this decrease in the explosion temperature of these samples occur with increase in the confinement volume is not clear. But these results show that it is fallacious to assume that ammonia liberating substances under all conditions would stabilize ammonium nitrate, zinc oxide, however, was found to stabilize ammonium nitrate under various confinement volume and increased its explosion temperature.

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The compound formed by the reaction between guanidine and dipicrylamine (hexanitrodiphenylamine) has been subjected to infrared analysis and x-ray diffraction studies. The behaviour of the bands around 6μ region in the infra-red spectra of the compound suggests that the compound formation between guanidine and dipicrylamine occurs through the nitrogen of guanidine molecule. The powder diffraction data showed that the compound belongs to the monoclinic system and the cell dimensions for the complex is $a=9.141 \text{ \AA}$, $b=8.868 \text{ \AA}$, $c=6.766 \text{ \AA}$ and $\beta=107^\circ 39'$. The space group is P_2/mC'_{2h} with two molecules per unit cell.

Structural Studies on Guanidine-Dipicrylamine Compound

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Introduction

It has been reported earlier¹ that dipicrylamine (hexanitro diphenylamine) forms a compound with guanidine and the method has been successfully utilized for the gravimetric estimation of guanidine in the presence of common contaminants like ammonium nitrate, urea, dicyandiamide etc. However, the inner structure and the nature of bonding in this compound had not been definitely determined. An attempt has been made in the present investigation to elucidate the nature of bonding and crystallographic properties of this compound.

Experimental

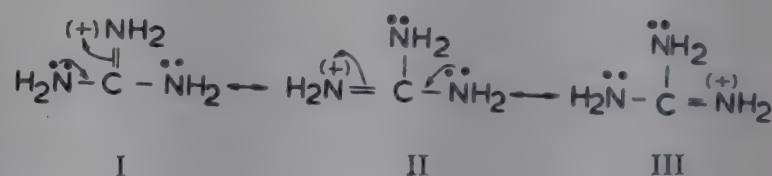
The purified and recrystallised samples were subjected to infrared and x-ray studies. For the former KBr pellets were prepared following a nearly similar procedure described by Ingebrigtsen et al². The spectra were recorded from 2.5 to 18μ using a scanning speed of 17 min. for the full range and using Perkin Elmer 421 dual grating IR. Spectrophotometer. X-ray diffraction patterns of the compound were obtained in a Philips Camera (cassette diameter 11.46 cm.) with $\text{CuK}\alpha$ radiation using nickel filter at 40 KV and 20 mA giving 6 hours of exposure to the sample. The sample was also run on the Philips x-ray diffractometer PW 1050/51. The interplanar distances were calculated from measurement on x-ray diffraction patterns with maximum accuracy. The phase identifications were done by the usual method of Hanawalt et al³.

Results and Discussions

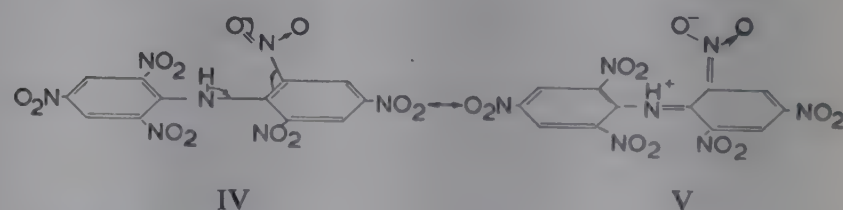
The IR absorption curves of dipicrylamine, guanidine

nitrate and guanidine-dipicrylamine are reproduced in Figs 1, 2 and 3 and the probable assignments of bands are given in Table 1.

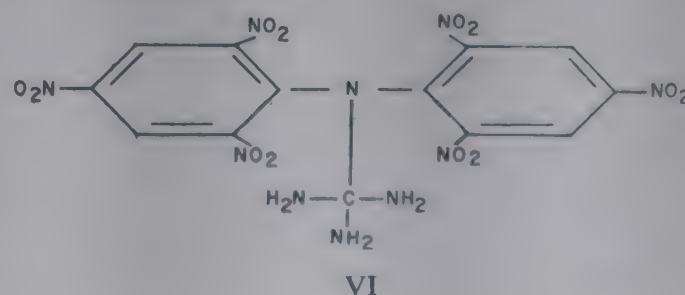
The structure of guanidinium ion involves resonance between the following forms.



Dipicrylamine has a number of resonating forms of which the following two forms contribute predominantly to the resonance.



It has been discussed in an earlier communication¹ that the compound forms a definite compound with dipicrylamine. The probable structure of the compound may be represented as follows:



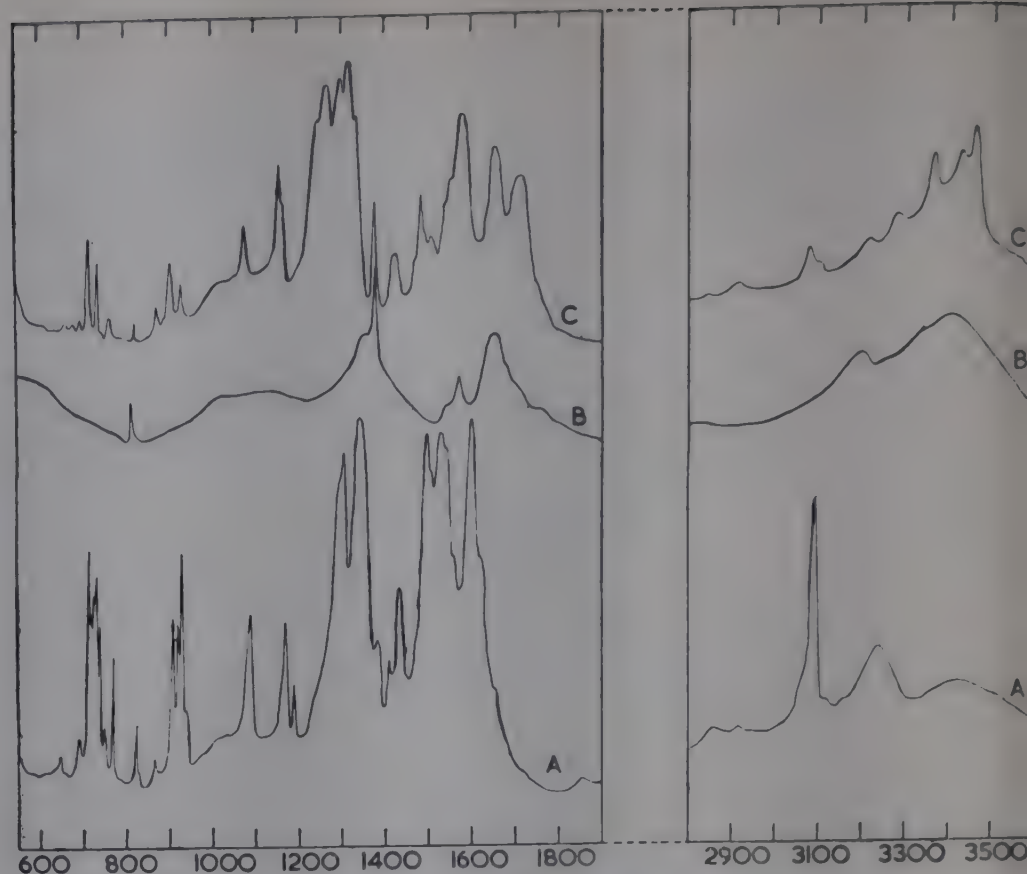
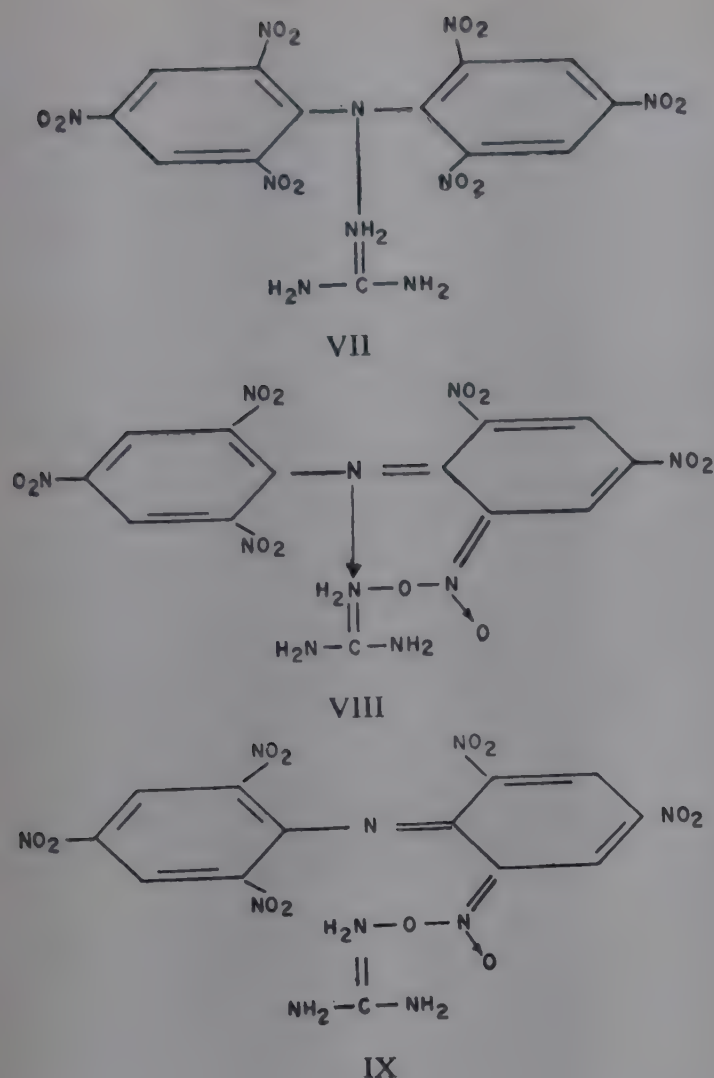


Fig. 1—Infrared Absorption Spectra
 A—Dipicrylamine
 B—Guanidine Nitrate
 C—Guanidine Dipicrylamine

3 μ Region: From an examination of a large number of compounds containing NH_2 or NH group, which has been carried out by earlier workers⁴ it is evident that when an NH_2 or NH group is involved in chelation or hydrogen bonding, the characteristic stretching frequency will be shifted to lower wave lengths and broadened. The compound exhibits number of bands in the 3 μ region and some of the bands are at lower N-H stretching frequency than the reagent itself.

The possibility that some of these bands are the first harmonics of the bands around 6 μ region is not likely for the extinctions of the bands at 3 μ are much too high compared with those at 6 μ to be harmonics of the latter. The symmetrical and antisymmetrical stretching vibrations of NH_2 groups would give rise to two bands separated by 100 cm^{-1} or less but some of the bands observed in the spectra of the compound are considerably further apart. In the case of this type of nitrogenous compounds, different types of hydrogen bonding (both inter and intramolecular) are possible and presence of multiple peaks may account for the same. The interpretation of the spectra in this region is further complicated by the presence of number of NH_2 groups. Hence, it is difficult to ascertain from the lowering of NH stretching frequency in this case, whether the peaks

arise from inter or intramolecular hydrogen bonding or chelation.

However, some of these bands have been assigned according to the earlier observation on the reagents^{6,7}. The infra-red band observed at 3425 cm^{-1} assigned to the N-H stretching in the spectrum of diphenylamine is observed at the same frequency in the spectra of the compound. The 3460 cm^{-1} band in the compound which is absent in both the reagents is assigned as asymmetrical NH stretching frequency indicating more freedom of NH_2 groups in the compound than in guanidine where considerable interaction between adjoining molecules occurs. An additional medium intense band at 3365 cm^{-1} is observed in the compound. This band is NH stretching vibration of guanidine which is lowered in the compound due to intermolecular hydrogen bond formation.

6 μ Region: The compounds have bands in the 6 μ region and these could arise from C-N stretching, N=O stretching in nitro, N-H bending, aromatic ring vibration and substitutions. The C=N stretching vibrations would be expected to give rise to most intense bands. In the type of molecule under study, the bands resulting from N-H bending and aromatic ring could affect the C=N stretching frequency due to coupling, since there is a common region around 6 μ where these bands may overlap. The C=N stretching bands usually occur at shorter wavelengths than the nitro bands.

TABLE 1—ABSORPTION MAXIMA OBSERVED FOR DIPICRYLAMINE, GUANIDINE NITRATE AND GUANIDINE DIPICRYLAMINE-COMPOUND AND THEIR ASSIGNMENTS, CM⁻¹

Dipicrylamine	Assignment [†]	Guanidine Nitrate*	Assignment	Guanidine dipicrylamine comp.	Assignment
3425 m, br	NH stretching (free)	3410 s, br	NH stretching	3460 s 3425 s 3365 s 3280 m 3215 m 3110 w 3085 m	NH stretching
3245 ms, br	NH stretching	3200 s	NH stretching		
3095 s, sp	=C-H stretching				=C-H stretching
1655 w, sh		1655 s	C=N stretching	1715 s 1655 s	C=N stretching (Ph-N=C) C=N stretching (C=NH ₂)
1623 m, sh	C=C skeletal				
1602 vs, sp					
1588 m, sh	NH bending	1577 ms	NH bending	1580 s	NH bending (un-co-ordinated)
1543 s, sh	C=C skeletal			1555 s, sh	NH bending (co-ordinated)
1530 vs, sp	C-N asym stretching (C-NO ₂)			1540 m, sh	NH bending coupled with C-N asym stretching (C-NO ₂)
1505 m, sh				1510 m	
1498 s, sp	Benzene ring substitutions and			1486 ms, sp	
1435 ms	C=C skeletal			1426	C=C skeletal and Benzene ring substitutions.
1411					
1411 m					
1385 m		1385 vs, sp	NO ₃ ⁻	1380 ms, sp	NO ₃ ⁻
1345 vs	C-N sym stretching (C-NO ₂)	1355 s, sh		1337 s, sh	C-N sym stretching (C-NO ₂)
1307 s, sp	CN stretching (C ₆ H ₅ -NH)			1319 vs	CN stretching (C ₆ H ₅ -N)
1300 s, sh	Ionic nitrite			1302 vs	Ionic nitrite
				1270 vs	Sym NO ₃ ⁻ stretching (co-ordinated)
				1250 s, sh	
1193 m, sp	Benzene ring substitutions			1165 m, sh	Benzene ring substitutions CH in plane deformation.
1170 ms	CH in plane deformation			1158 s, sp	
1091 ms	Benzene ring breathing			1080 m	Benzene ring breathing.
943 w, sh				934 w	Benzene ring substitutions (?)
931 s, sp	Benzene ring substitutions (?)				
923 m, sp				910 m	
910 ms, sp				878 w	C-N sym stretching (C-NO ₂)
868 w	C-N sym stretching (C-NO ₂)/CH out of plane vibration.				
827 m, sp	CH out of plane deformation for two free H	810 m	NO ₃ ⁻	825 w	NO ₃ ⁻ /CH out of plane deformation for two free H.
772 ms, sp	NH ₂ rocking			766 w	NH ₂ rocking
751 w				740 m, sp	C-N stretching (C-NO ₂)
741 w	C-N stretching (C-NO ₂)				
734 ms, sp					
729 ms, sp				720 m, } sp	Benzene ring substitutions out of plane CH vibrations.
723 m, sp	Benzene ring substitutions out of plane CH vibrations.			700 w }	
717 s, sp					
691 w,					
650 w					

NOTE: vs—very strong, s—strong, ms—medium strong, m—medium, w—weak, br—broad, sh—shoulder, sp—sharp.

†Taken from Bellamy⁶, and Hadzi et al⁷.

*Assignments have been made in accordance to Lieber et al⁸.

Lieber et al⁵ have published the spectra of 38 guanidine derivatives and quoted an overall range of 1580-1657 cm^{-1} for the $\text{C}=\text{N}$ group for this type of compounds. Basing, on this observation, the absorption peaks observed in the spectra of the compound at 1655 and 1580 cm^{-1} are, therefore, assigned to $\text{C}=\text{N}$ stretching and $\text{N}-\text{H}$ bending frequency respectively. It appears therefore, the $\text{C}=\text{N}$ stretching frequency of guanidine molecule does not change on compound formation with dipicrylamine, which suggests that compound formation does not take place through the carbon in the guanidine (as suggested in structure—VI). If compound formation took place through the carbon atom, bond between amine nitrogen and the carbon atom would have acquired single bond character, resulting in a lowering of the $\text{C}-\text{N}$ frequency. So it may be inferred that compound formation takes place through the nitrogen atom of guanidine. From a comparison of free guanidine nitrate molecule and the compound, it can be seen that in addition to 1580 cm^{-1} band similar to that found in the spectra of guanidine one band at lower frequency 1555 cm^{-1} appeared in the spectra of the compound. The band at 1580 and 1555 cm^{-1} in the spectra of the compound can be considered to arise from the free NH_2 bending and co-ordinated NH_2 bending vibrations respectively. Three different structural configurations as shown in figure VII, VIII and IX may be conceived on this basis.

A medium strong band at 1715 cm^{-1} was found in the spectra of the compound (Fig. 3) which is absent in both guanidine and dipicrylamine. To facilitate an understanding of this frequency in the spectra of the compound, the vibrational assignments in the 6-8 μ region of dipicrylamine are discussed first.

The spectra of dipicrylamine (Fig. 1) shows distinct bands at 1530 cm^{-1} in addition to a number of bands between 1411-1655 cm^{-1} . In diphenylamine and related compounds^{4,6,7} the bands in this region are due to benzene ring vibrations, ring-substitutions and NH bending mode. Following their observations the bands in the dipicrylamine referred above have been assigned accordingly (Table 1). The band at 1530 cm^{-1} is known to be due to $\text{C}-\text{NO}_2$ (asym.) stretching in aromatic nitro compounds. The NH deformation mode, which appeared at 1588 cm^{-1} in dipicrylamine has been lowered to 1540 cm^{-1} in the compound due to compound formation.

The aromatic ring vibration around 1600 cm^{-1} in dipicrylamine is absent in the compound and a new medium strong band at 1715 cm^{-1} appeared in the compound as has been stated earlier. This band seems

too high in frequency to be assigned to aromatic ring vibration only. However, in the type of compound having structure $\text{Ph. N}=\text{C}$ which contains $\text{C}=\text{N}$ link, an additional band around 1670 cm^{-1} besides that corresponding to aromatic vibration have been observed and assigned as $\text{C}=\text{N}$ vibration by the other workers^{6,8}. Accordingly it seems therefore, reasonable to assign the band at 1715 cm^{-1} to $\text{C}=\text{N}$ coupled with aromatic ring vibration. Further the absence of the band in the 1600 cm^{-1} associated with the linkage $\text{N}-\text{C}-\text{Ph}$ and appearance of this new band at 1715 cm^{-1} assigned to $\text{N}=\text{C}-\text{Ph}$ in the compound is quite possible because of the faster rate of reaction of the guanidine nitrate with the enolic form of dipicrylamine (v) in preference to

TABLE 2—FINAL AGREEMENT OF OBSERVED AND COMPUTED Q_{hkl} 's FOR GUANIDINE AND DIPICRYLAMINE COMPOUND

Powder diagram line	dÅ	I	Qobserved	Qcalculated	hkl
1.	8.74	ms	0.0130	0.0131	100
2.	7.95	w	0.0158	0.0162	010
3.	6.56	vw	0.0232	0.0241	001
4.	4.98	w	0.0403	0.0403	011
5.	4.39	vw	0.0518	0.0524	200
6.	4.28	vw	0.0546	0.0549	201
7.	4.04	ms	0.0612	0.0642	111
8.	3.91	vw	0.0632	0.0648	020
9.	3.67	w	0.0742	0.0711	21 $\bar{1}$
10.	3.57	vw	0.0785	0.0779	120
11.	3.39	s	0.0870	0.0879	10 $\bar{2}$
12.	3.17	vw	0.0995	0.0964	002
13.	3.03	w	0.1089	0.1096	30 $\bar{1}$
14.	2.89	vw	0.1197	0.1179	300
15.	2.770	vw	0.1303	0.1311	102
16.	2.728	ms	0.1344	0.1341	310
17.	2.612	vw	0.1466	0.1458	030
18.	2.516	vw	0.1580	0.1589	130
19.	2.391	vw	0.1749	0.1744	301
20.	2.335	vw	0.1834	0.1827	320
21.	2.257	w	0.1963	0.1959	122
22.	2.174	vw	0.2116	0.2169	003
23.	2.073	vw	0.2327	0.2331	013
24.	2.029	vw	0.2429	0.2422	032
25.	1.955	vw	0.2616	0.2624	103
26.	1.883	vw	0.2820	0.2817	023
27.	1.836	vw	0.2967	0.2969	40 $\bar{3}$
28.	1.803	vw	0.3076	0.3072	141
29.	1.782	vw	0.3149	0.3141	24 $\bar{1}$
30.	1.689	vw	0.3505	0.3503	213
31.	1.676	vw	0.3560	0.3556	042
32.	1.564	vw	0.4088	0.4082	133
33.	1.490	vw	0.4504	0.4504	024
34.	1.444	vw	0.4796	0.4799	233
35.	1.363	vw	0.5383	0.5382	432

that with the other form (iv). Hence the structure (vii) which involves N-C-Ph linkage is excluded from consideration.

Amongst the rest two forms structure VIII was conceived in analogy with K-dipicrylamine structure⁹. However, this proposition is not tenable from the electronic configuration of the molecule as the nitrogen atom of the guanidine part, having no vacant shell, can not act as an acceptor of the lone pair of electrons from the nitrogen of dipicrylamine. Structure (IX) amongst the possible configurations well conforms with the above data. In this structure, N of the dipicrylamine has a free lone pair of electrons. These electrons may have a tendency to be attracted towards the positively charged N of the guanidine. The very weak lines in the 3 μ region tends to support this view. This may explain the properties of the compound e.g. low solubility in water, high solubility in acetone, non-formation of methyl-iodide derivative etc.¹²

X-ray Data: The interplanar spacing and corresponding Q values ($Q_{hkl}=1/d^2_{hkl}$) are listed in Table 2. Attempts were made to index the powderlines with cubic, tetragonal and hexagonal system and the data did not fit with any one of these systems of higher symmetry. In such case the powder pattern was indexed by Ito's method¹⁰ and the procedure for determining the reciprocal cell have already been described.¹¹

The first three lines in Table 2 was selected as Q_{100} , Q_{010} and Q_{001} . It can be seen that the observed Q's are in quite agreement with the calculated Q values for other higher orders of reflection.

In order to select the reciprocal cell angles (hko) (hol) and (okl) reflections were carefully examined and it was found that (hko) and (okl) reflections were present if α^* and γ^* were taken to be 90°. The angle β could then be calculated after studying some pairs of (hol) and (hol⁻) reflection according to the equation.

$$\cos \beta^* = \frac{Q_{hol} - Q_{hol^-}}{4hla^*c^*}$$

The dimensions of the reciprocal cell then becomes,
 $a^* = 0.1148$ $a^* = 90^\circ$
 $b^* = 0.1271$ $\beta^* = 72^\circ 21'$
 $c^* = 0.1551$ $\gamma^* = 90^\circ$

Finally, the other Q_{hkl} values were determined using the equation;

$$Q_{hkl} = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hka^*b^* \cos \gamma^* + 2klb^*c^* \cos \alpha^* + 2hlc^*a^* \cos \beta^*$$

The direct cell dimensions are as follows:

$a = 9.141 \text{ \AA}$ $a = 90^\circ$
 $b = 7.868 \text{ \AA}$ $\beta = 107^\circ 39'$
 $c = 6.766 \text{ \AA}$ $\gamma = 90^\circ$

The crystal therefore belongs to the monoclinic system. The indexed powder pattern did not show any evidence of screw axes and glide planes. The probable space group may be $P 2_1/m-C_{2h}^1$.

The observed density of 3.606 g. cm.⁻³ indicates two molecules per unit cell; calculated density = 3.567 g. cm.⁻³

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The prediction of phase equilibria is a problem encountered in the calculation of any non-ideal multi-component distillation. As a typical case, this paper describes the separation of isobutylene from methyl- and vinylacetylene with dimethyl-formamide as an extractive agent in a continuous distillation column. It contains the calculation of phase equilibria and the vapour phase correction factors, the sources and the evaluation of other thermodynamic data, and as a result the theoretical number of plates under varying conditions obtained from computer ZRAI.

On the Calculation of a Multicomponent Extractive Distillation

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In Leuna Werke (Germany),¹ a hydrocarbon stream consisting of isobutylene, methylacetylene and vinylacetylene was to be separated. The first two components were of close boiling points so that it was uneconomical to separate them by ordinary means. Preliminary investigations in the Works laboratory had revealed that dimethyl formamide—a solvent of an entirely different chemical nature and of a very low volatility—when added to this hydrocarbon feed mixture could sharply alter the relative volatility of these components. These laboratory investigations were supplemented by calculations with computer ZRAI and a great difference in departure from ideality between the solvent and these two components was found.

Problem

A feed consisting of 60 mol. per cent isobutylene, 13 mol. per cent methylacetylene and 27 mol. per cent vinyl acetylene was to be separated with the aid of the extractive agent, dimethyl formamide. The overhead product was not to contain more than 0.5 per cent methylacetylene and the bottom product not more than 0.5 per cent isobutylene. It was required to investigate the influence of reflux ratio on the theoretical number of plates and the composition at the individual plates. The column worked without a dephlegmator and the top pressure was to be so chosen as to permit condensation of the vapours with process cooling water.

Main Assumptions: (1) Since p - x curves for all binary mixtures were not known, it was assumed that the combinations C_3H_4 - C_4H_4 ; C_4H_8 - C_3H_4 and C_4H_8 - C_4H_4

behave ideally; (2) the influence of temperature on activity co-efficients was neglected.

Thermodynamic Data

1. **Determination of Activity and Fugacity Co-efficients:** The activity coefficients for the binary mixtures were calculated by the Tao¹ method and balanced with Redlich—Kister equation². The vapour phase corrections were obtained from the equation proposed by Scheibel³. On the basis of data obtained in the laboratory for p - x at constant temperature for the binary solutions, viz. C_3H_7NO - C_4H_8 , C_3H_7NO - C_3H_4 and C_3H_7NO - C_4H_4 , p - x curves were plotted and $\left(\frac{\delta P}{\delta x}\right)$ at $x=0$ measured.

Since a computer programme for determining the above-mentioned values was already available*, it was necessary only to measure the vapour pressure of the mixture in relation to mol. fraction in liquid, T_r , P_{kr} and P° . The molal integral volumetric change of solutions Δ_v was not considered and an approximate form of the equation derived by Gautreaux and Coates⁴.

$$\gamma_{1.0} = \frac{P}{P_1^0} \left[1 + \left(\frac{\delta P}{\delta x_1} \right)_T \left(\frac{1}{P} \right) \right] \quad \dots (1)$$

was used.

The necessary critical data were taken from Lehman charts⁵. A constant factor $f(T_r) = 0.08$ was substituted for the vapour phase correction.

* Computer centre: VEB Leuna Werke, Walter Ulbricht, E. Germany

$$\ln \Phi = \frac{P_1^0 - P}{P_{kr}} \left[f(Tr) - \frac{0.197}{T_{kr}} + 0.012 + \frac{0.4}{T_r^2} + \frac{0.146}{T_r^{4.27}} \right] \quad \dots \quad (2)$$

The Redlich-Kister constants B, C and D were obtained from the following equations developed in the computer centre of Leuna Werke††

$$\ln \gamma_2 = x_1^2 [B + C + D - (4C + 8D) x_2 + 12D x_2^2] \quad \dots (3)$$

$$\ln \gamma_1 = (1 - x_1)^2 \{B - C + D + (4C - 8D) x_1 + 12D x_1^2\} \quad \dots (4)$$

The deviation between the values obtained by Tao and Redlich-Kister equations was minimized by the method of the least squares. With these vapour phase and activity coefficient correction factors, p-x curves were reproduced.

From Fig. 1, it can be seen that there is a maximum of 2 per cent deviation from the experimentally determined values. Hence these values were accepted for determining the activity co-efficients for the four component mixtures using the extended equation of Redlich-Kister².

$$\log \gamma_1 = \sum_k x_k [B_{1k} + (x_1 - x_k) \{2C_{1k} + 3D_{1k} (x_1 - x_k)\} + x_k \{(C_{1k} + 2D_{1k}(x_1 - x_k))\} - \frac{1}{2} \sum_j x_j \sum_k [B_{jk} + (x_j - x_k) \{2C_{jk} + 3D_{jk}(x_j - x_k)\}] \quad \dots (5)$$

2. *Latent Heat of Evaporation:* From available data on isobutylene and dimethyl formamide values for methyl and vinyl acetylene were calculated by the methods proposed in Lehman Mappe⁵.

$$r_s = \Phi(T_s), \quad \frac{M_{rs}}{T_s} = 22 \dots (\text{Trouton's rule}) \quad \dots (6)$$

$$\frac{M_r}{T_{kr}} = \frac{AR}{M_{lg}} \frac{(1 - P/P_{kr}) \cdot \log P_{kr}/P}{(T_{kr}/T - 1)} \quad (\text{Cederberg equation}^5) \quad \dots (7)$$

and also from the Clausius—Clapeyron⁵ equation with the comparative data of a standard substance.

$$M_r = \frac{T_{mb} T_{kr}}{T_{krb}} \frac{\frac{1}{T_{rb}} - 1}{\frac{1}{T_r} - 1} \quad \dots (8)$$

(In this equation b refers to reference substance)

†† unpublished

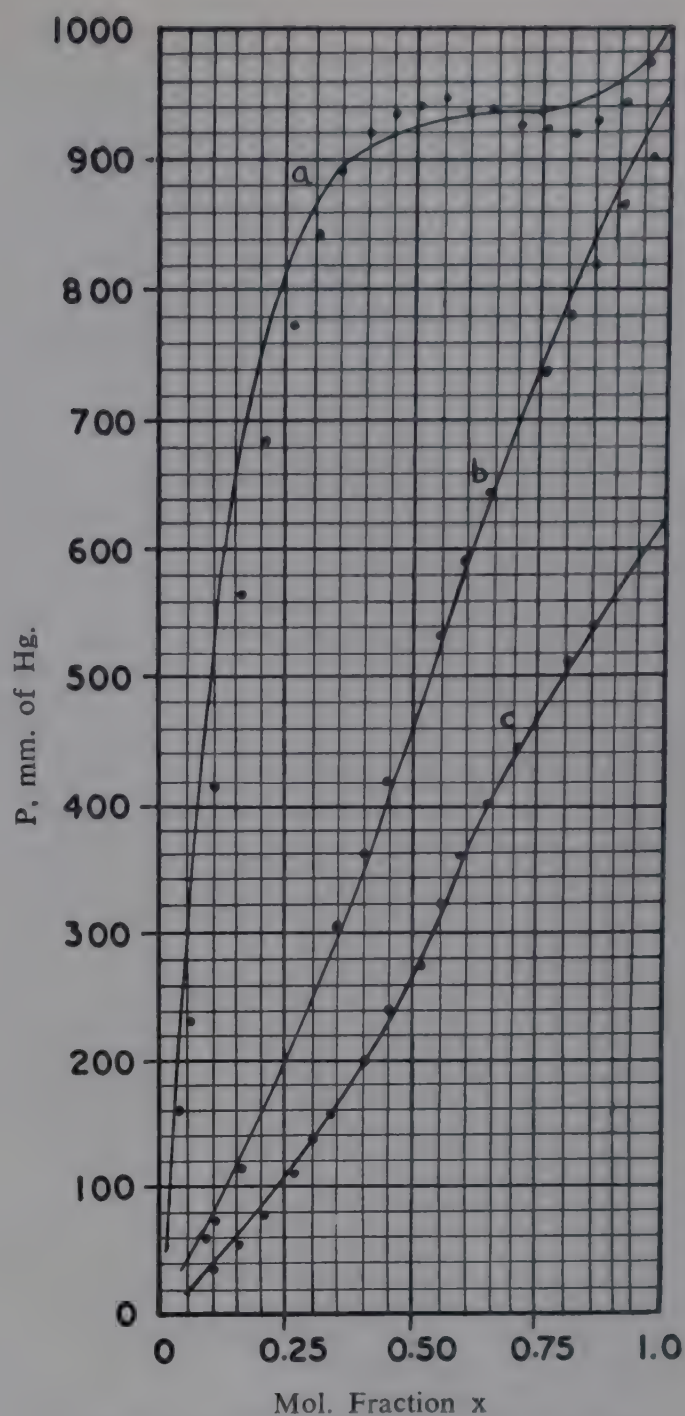


Fig. 1—Pressure Vs Mol fraction Curves

Where O₂ and C₂H₄ were used as reference substance. The Cederberg and the modified Clausius—Clapyron equations gave tenable values.

The dependence of latent heat on temperature was calculated from the following equation⁵

$$\ln M_r = \ln r_m + n_0 \ln \left(1 - \frac{T}{T_{kr}} \right) \quad \dots (9)$$

3. *Specific Heat:* Values for methyl and isobutylene were obtained from Wärme Atlas and Rosini⁵. Dimethyl formamide data were obtained from the laboratory (Table 1). For vinyl acetylene, C_p was calculated from the molecular structure by the method proposed by Sakiadis and Coates⁶. As a check, C_p values for dimethyl

TABLE 1—CRITICAL DATA & CONSTANTS FOR CALCULATING VAPOUR PRESSURE, HEAT OF VAPORIZATION & SPECIFIC HEATS AT VARYING TEMPERATURES

	Isobutylene	Dimethyl-Formamide	Methyl Acetylene	Vinyl Acetylene
P _{cr} mm. Hg	30,000	19,215	32,482	57,000
T _{cr} °K	417.5	597	400.9	458
a	15.8	17.2	15.904	16.58
b	2125	4070	1905	2235
c	240	230	230	230
C _a	19.9	30.6	13.75	17.85
C _b	0.0532	0.0511	0.0296	0.0375
ln V _m	8.95	9.54	8.85	9.27
n ₀	0.371	0.354	0.349	0.358

acetylene and methyl acetylene were calculated by this procedure. A deviation of 30 per cent from the values given in literature was found. Therefore, for technical purposes the specific heat (Kcals/kg°C) of methyl-acetylene was assumed the same as that for vinyl acetylene. C_p at different temperatures was evaluated from the following equation⁵

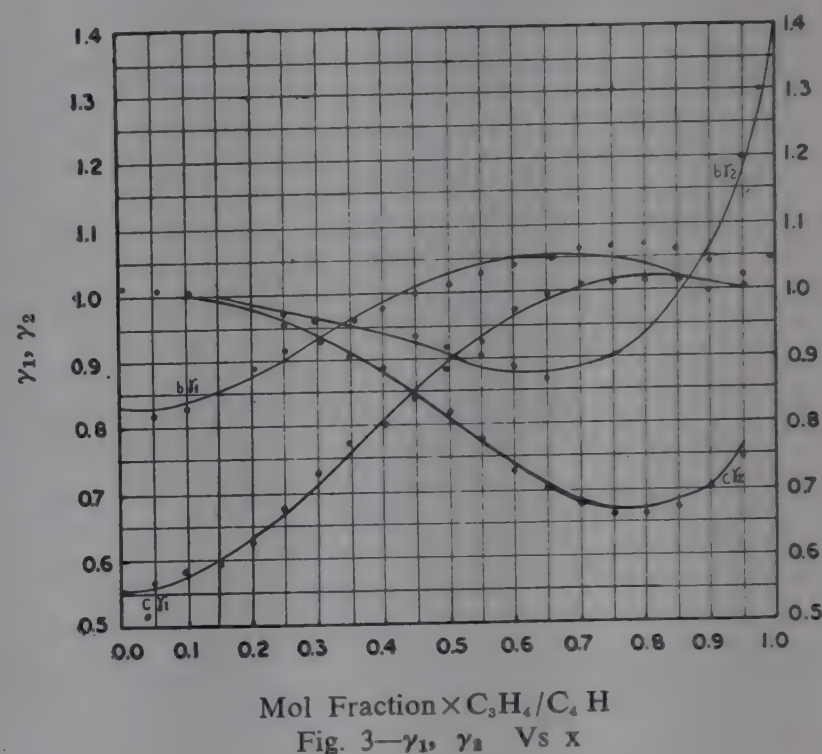
$$C_p = C_a + C_b t \quad \dots(10)$$

4. *Vapour Pressure of Pure Components:* These data were obtained from the Antoine equation, viz.

$$\ln P = a - \frac{b}{t+c} \quad \dots(11)$$

For determining the constants a and b, lines were drawn between the normal boiling point and the critical point

on a $\ln P, \frac{1}{t+c}$ diagram.

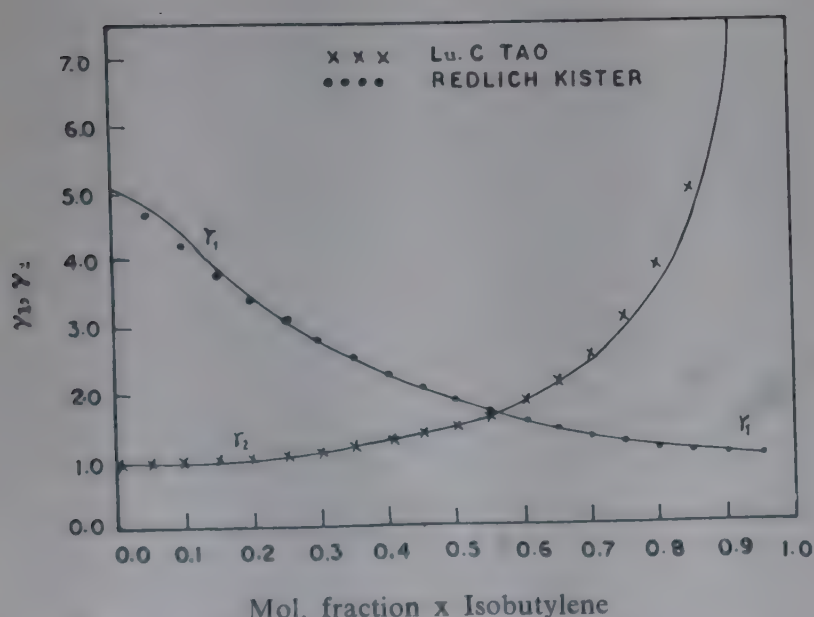


Calculation of Number of Plates

A block diagram of the computer programme on distillation of non-ideal multicomponent solutions is seen in Fig. 4. For the digital computer ZRA1, a detailed programme has been prepared by Mathematiker Weinelt⁶. Here some observations made while investigating various variables are reported.

1. *Vapour Phase Concentration of Extractive Material at the Top:* For the material balance calculations dimethyl formamide in the tops was assumed to be 0.05 mol. per cent. A lower figure would work out unfavourably, because thereby the necessary number of plates increases further. A higher concentration gives a mixture at top that is very rich in dimethyl formamide which leads to losses and low top pressure.

2. *Feed Plate Location:* A commonly applied test, viz.



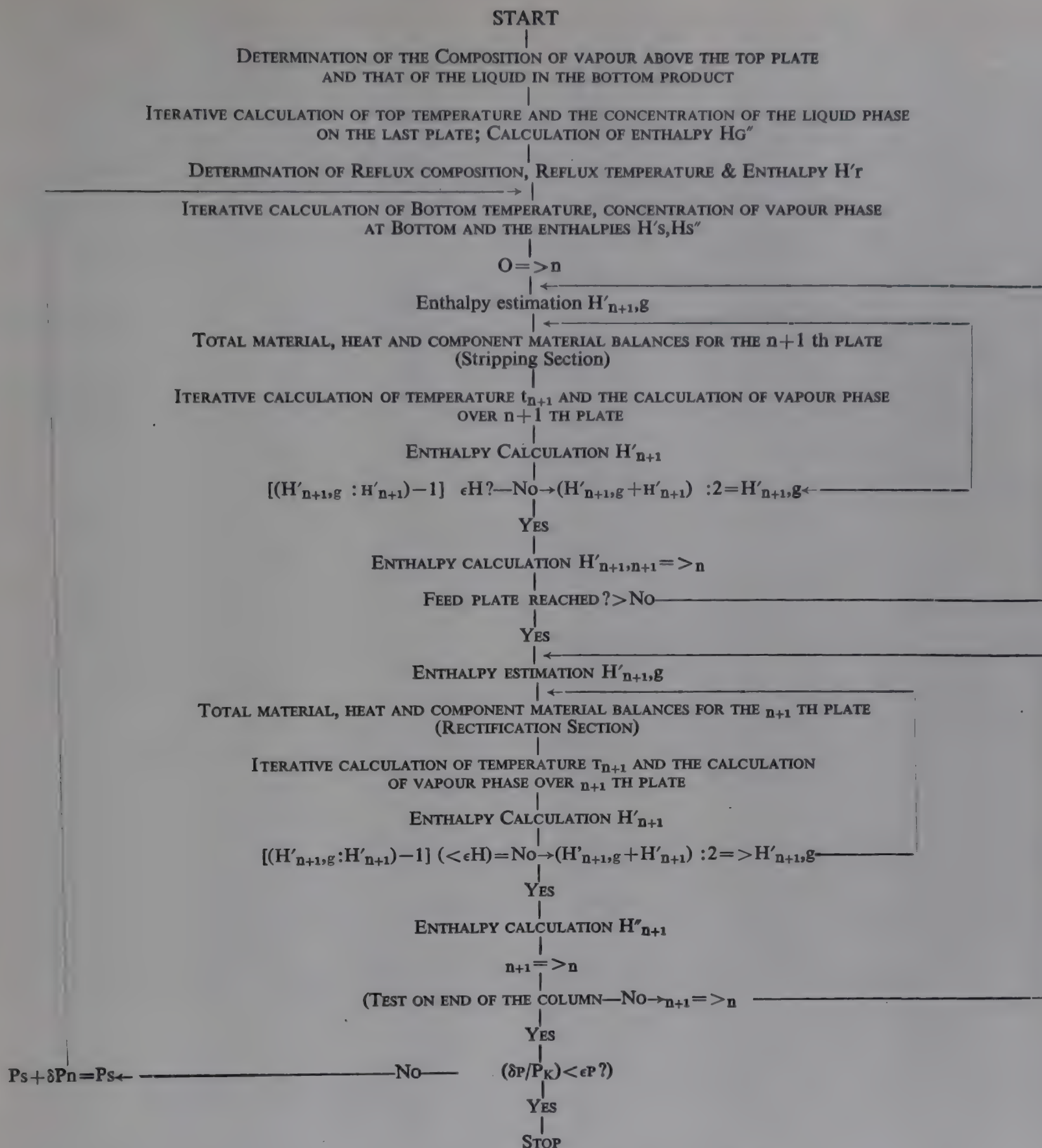


Fig. 4—Block Diagram: Non-ideal Multi-component Distillation

specification of a particular concentration of the lighter component i —(C_4H_8), was tried but found not effective since it was difficult to make a meaningful estimate. Another test using a fixed value for the concentration

ratio of the key components $\frac{x_{s1}}{x_{s2}}$ was successful.

3. *Enthalpy Estimation:* Owing to the extremely large difference between the relative volatilities of dimethylformamide and other components, temperature of the liquid drops sharply from the bottom to the first plate. For instance, when the bottom temperature is 123°C , the temperature of the liquid leaving the first plate is 56°C . Hence, enthalpy estimation by the equation,

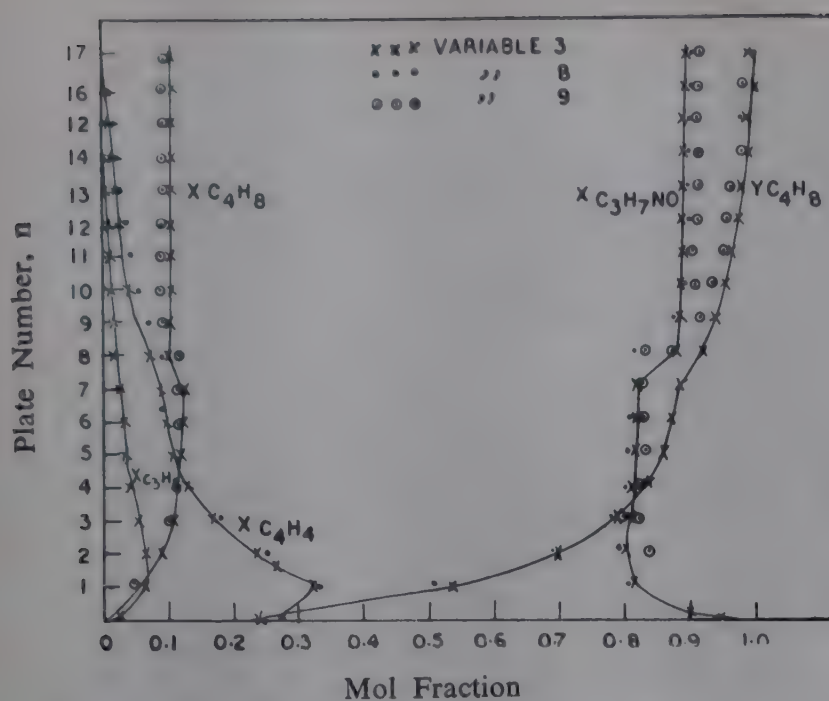


Fig. 5—Liquid and Vapour Composition Vs Plate Number

$2H'_n - H'_{n-1} \Rightarrow H_{n+1}$, leads to a negative figure. As a result $H'_n \Rightarrow H_{n+1}$ was used.

4. *Influence of Reflux Ratio and the Composition at the Top Plate on Number of Plates:* The reflux ratio and the quantity of external reflux which permitted the necessary separation were determined by trial calculations. The minimum product reflux could be estimated by the following material balance equations.

$$G_n Y_{n1} + S_{X_{S1}} - E_{X_{E1}} : L_{n+1} \Rightarrow X_{n+1} \quad \dots (12)$$

X_{n+1} should be > 0

To start with, the composition of the reflux was kept constant and its ratio with top pressure varied. The investigated range gave only in a few cases useful results. So, for example, the variable 3 (Table 2) led to 17 plates when the external reflux amounted to 800 K. mol/hr. With the same composition and 700 K. mol/hr. the feed

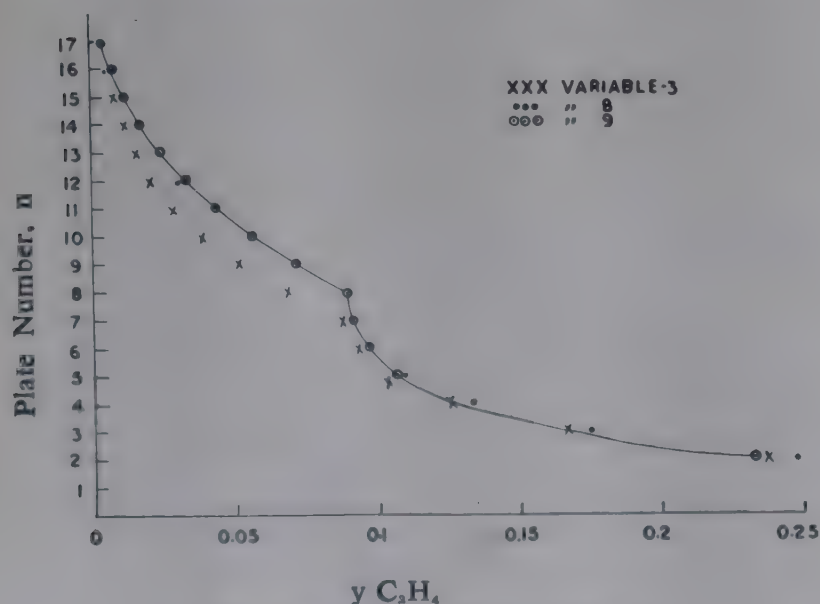


Fig. 6— yC_3H_4 Vs Plate Number

TABLE 2—VARIATION PROGRAMME

No.	Z (K. mol) External Reflux	V Reflux ratio	n Number of plates	Remarks
1a	200	3.7	—	Interruption due to $X_{n+1}C_4H_6 < 0$
1b	200	3.9	—	"
1c	300	5.8	—	"
2	600	12	—	Feed test not fulfilled
3	800	15.5	17	
4	900	17.45	—	$T_s > TK_{rC_3H_4}$
5	700	13.56	—	Feed test not fulfilled
6	900	17.45	—	$T_s > TkrC_3H_4$
7	850	16.47	—	$T_s > TkrC_3H_4$
8	750	14.52	17	
9	800	15.20	17	

2. Redlich-Kister Constants

$$B_{21} + 2.0259 C_{21} - 0.4658 D_2 + 0.0979$$

$$B_{23} - 0.1341 C_{23} + 0.2568 D_{23} + 0.2058$$

$$B_{24} - 0.6354 C_{24} + 0.2080 D_{24} + 0.2638$$

plate could not be reached. With 900 K. mol/h, the bottom temperature rose above the critical temperature of methyl acetylene.

The equation for calculating the vapour phase corrections according to Scheibel is, however, valid only upto the critical temperature, so the computations had to be given up. At 750 K. mol/hr. external reflux, the same plate numbers were obtained. Alteration of reflux composition (variable 10) brought no change of plate number. From the investigated variables is seen that by the given product purities, the reflux quantity and the plate number hardly change and therefore the product reflux can be held low.

Nomenclature

a, b, c	Constants in the Antoine equation.
γ	Activity Co-efficient
Φ	Vapour phase correction factor.
P	System pressure in mm Hg.
P°	Vapour pressure of pure components
P_{kr}, T_{kr}	Critical pressure & Critical temperature.
BCD	Redlich-Kister equation constants.
M_r	Molal heat of evaporation.
M_{rb}	Molal heat of evaporation of reference substance.
T_r	Reduced temperature
T_b	Boiling temp. (K°) at 760 mm. Hg.
t	Temperature, °C

M	Molecular weight
r	Heat of vaporisation at temperature T
R	Gas constant
A	Mechanical Equivalent of Heat $\times 1/427 \frac{\text{K. Cal}}{\text{M. Kg.}}$
$V_m N_o$	Constants for determining Molal heat of vaporization at varying temp.
C_a, C_b	Constants in the equation for determining molal specific heat of liquid at varying temp.
Mlg	$\frac{1}{2.3026}$
$\bar{x}_{s1} \bar{x}_{s2}$	Mol. fraction of key components.
G	Quantity of vapour in K mol.
E	Feed quantity in K mol.
Z	External reflux in K mol.
K	Quantity of overhead product in K mol.
x	Mol. fraction in liquid phase.
y	Mol. fraction in vapour phase.
H	Enthalpy in Kcal/Kmol, based at 0°C.
δP	Pressure drop in a plate.

Indices

Index E	—refers to feed
Index S	—refers to bottom product.
Index K	—refers to overhead product.
Index Dash	—refers to liquid phase.
Index 2 Dashes	—refers to vapour phase.
Indexes i, j, k	—refer to values 1 to n.
Index n	—refers to plate n.

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Three surface samples of black, red and alkali soils were studied for retention and release of molybdenum in presence of a number of complexants at different doses. The effect of increasing the doses was found not very distinct on the retention values (R) of molybdenum. The following decreasing order of efficiency of the complexants in increasing retention of the added molybdenum was observed for black soil: aluminon > all others (which have similar effect, least effective being EDTA), and for alkali soil: aluminon > 8-hydroxyquinoline > EDTA (others have a similar effect). In red soil, however, they have a negative role.

Various complexants added to soils have variable effects in releasing applied molybdenum. Ammonium oxalate and EDTA appear to affect E/R—the ratio of extractable to retained molybdenum in soils—to a maximum extent leading to increased values. The increases are 4-37, 11-28 and 0-38 per cent in black, red and alkali soils respectively. The red and alkali soils are quite similar with respect to complexants in increasing E/R values, but the black soil behaves in two different ways—it gives increased E/R values with ammonium oxalate, sodium salicylate, 8-hydroxyquinoline and EDTA but with potassium thiocyanate and aluminon gives decreased values.

Effect of Complexants on Retention and Release of Molybdenum Applied to Soils under Water-Logged Condition

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No data are available on the effect of complexants on the retention and release of added molybdenum to soils. An effort was, therefore, made to find out the effect of complexants on the retention and release of molybdate ions using three different soils, viz. the black, red and alkali soils.

Experimental

Three surface samples—one each from black, red and alkali soils—were collected from an eastern district of U.P. for the purpose. Their chemical characteristics are given in Table 1.

In order to investigate the role of complexants on molybdenum retention and release, three doses 0.01, 0.02 and 0.05 per cent of the complexants, viz. ammonium oxalate, aluminon, potassium thiocyanate, sodium salicylate, 8-hydroxyquinoline and EDTA were added.

20 ml. of ammonium molybdate solution was added so as to make 10 ppm molybdenum in soil. The contents were shaken and then allowed to remain in contact for 45 days in test tubes, after which the supernatant liquid was filtered using suction. The whole of the filtrate was analysed for molybdenum using a colorimetric method¹.

The amount of molybdenum present in the blanks was also deducted in all the experiments. The difference between the amount initially added and that present in the filtrate was taken to be the amount of molybdenum retained by 2g. soil. It has been represented by a notation R.

Release of Retained Molybdenum: The residual soil samples after filtration were used for the study of molybdenum release. 20 ml. of Grigg's² acid ammonium oxalate reagent was used for the release of retained molybdenum by soils. The amount, thus released, has been denoted by E. The ratios of E and R have been calculated and given in Table 3. The unextracted molybdenum has been denoted by F i.e. fixed form.

Results and Discussion

Effect of Complexants on Molybdenum Retention: The effect of different complexants on molybdenum retention under water-logged condition is given in Table 2.

Effect of Ammonium Oxalate: The R values increase with increase in the concentration of oxalate ions in

TABLE 1—CHEMICAL CHARACTERISTICS OF THE SOILS

Soil	Name of Place	Name of District	pH	Sesqui-oxides, %	Total Carbonates as CaCO ₃ , %	Organic Carbon, %	Total Mo, ppm
Black	Babuganj	Allahabad	7.5	16.72	2.75	0.40	2.37
Red	Meja	-do-	7.5	7.60	1.45	0.60	3.00
Alkali	Soraon	-do-	7.9	—	1.07	0.58	1.25

TABLE 2—EFFECT OF WATER-LOGGING ON MOLYBDENUM RETENTION IN PRESENCE OF COMPLEXANTS (R VALUES)
(Mo added: 10 ppm.)

Treatments	Soils		
	(Black) Babuganj	(Red) Meja	(Alkali) Soraon
Control	4.00	9.00	4.00
Ammonium oxalate, %			
0.01	4.00	9.00	4.50
0.02	4.50	9.00	4.50
0.05	4.50	9.00	4.00
Aluminon, %			
0.01	6.50	9.00	8.00
0.02	7.50	8.50	9.00
0.05	7.50	8.50	9.50
Potassium Thiocyanate, %			
0.01	5.00	9.00	6.00
0.02	4.50	8.50	5.00
0.05	4.50	8.50	5.00
Sodium Salicylate, %			
0.01	4.50	8.00	4.00
0.02	4.50	7.50	4.00
0.05	4.50	7.50	6.00
8-hydroxyquinoline, %			
0.01	4.50	8.50	7.00
0.02	4.50	8.50	8.00
0.05	4.50	8.50	8.00
EDTA, %			
0.01	3.00	8.50	6.00
0.02	3.00	8.50	6.00
0.05	3.00	8.50	6.00

black and alkali soils alone but the increases are not very marked.

Effect of Aluminon: There is an increase in R value in black and alkali soils with no distinct change in red soil. However, the increases are higher than those obtained with ammonium oxalate.

Effect of Potassium Thiocyanate: Its behaviour is like that of ammonium oxalate. The retention shoots high

at lower concentration of the complexant and the concentration and the R value indicate negative correlation.

Effect of Sodium Salicylate: A distinct decrease in R value in red soil is observed. However, the effect is similar to that of ammonium oxalate with black and alkali soils.

Effect of 8-hydroxyquinoline: A distinct increase—100 per cent increase at 0.05 per cent concentration of complexant—in R value of alkali soil alone is observed.

Effect of EDTA: It induced decrease of R values in black and red soils but an increase in the alkali soil. With increased doses, there is no increase in R values.

Release of Molybdenum Retained Under Water-logged Condition: The results on the release of molybdenum retained under water-logged conditions in the presence of complexants are given in Table 3.

The complexants added along with molybdenum solution when allowed to remain in contact with soil for 45 days appear to affect E/R values of molybdenum. These values increase in most of the cases but they decrease in the case of black soil with two complexants viz. potassium thiocyanate (KCNS) and aluminon. The E/R values can increase only if E values are high or R values are low but it has been observed under retention studies that, in most of the cases, the complexants have helped in increasing R values of molybdenum. Hence, increased E/R values indicate that the retained molybdenum is present in soils in forms that are extractable by acid ammonium oxalate. In other words, the conversion of retained molybdenum into a fixed form is not encouraged in presence of complexants. Thus, the presence of complexants helps in retarding the fixation of added molybdenum in soils under water-logged conditions.

However, there are exceptions to it. The black soil shows decreased E/R in presence of potassium thiocyanate and aluminon. It is possible under the condition that the form in which molybdenum has been retained

TABLE 3—RELEASE OF MOLYBDENUM RETAINED UNDER WATER-LOGGED CONDITIONS IN PRESENCE OF COMPLEXANTS

Complexants Added, %	Black Soil (Babuganj)			Red Soil (Meja)			Alkali Soil (Soraon)		
	E	E/R	F/R	E	E/R	F/R	E	E/R	F/R
Control	2.50	0.63	0.37	6.50	0.72	0.28	2.00	0.50	0.50
Amm. Oxalate									
0.01	3.50	0.88	0.12	7.50	0.83	0.17	3.00	0.67	0.33
0.02	3.50	0.77	0.23	7.50	0.83	0.17	3.00	0.67	0.33
0.05	4.50	1.00	0.00	7.50	0.83	0.17	3.50	0.88	0.12
Aluminon									
0.01	3.00	0.47	0.53	8.00	0.89	0.11	3.50	0.44	0.56
0.02	3.00	0.40	0.60	8.50	1.00	0.00	4.50	0.50	0.50
0.05	2.00	0.27	0.73	9.00	—	—	4.50	0.53	0.47
Pot. Thiocyanate									
0.01	2.00	0.40	0.60	8.50	0.94	0.06	3.00	0.50	0.50
0.02	2.50	0.55	0.45	8.50	1.00	0.00	3.00	0.60	0.40
0.05	2.50	0.55	0.45	8.00	0.94	0.06	3.00	0.60	0.40
Sod. Salicylate									
0.01	2.50	0.55	0.45	7.50	0.94	0.06	2.50	0.63	0.37
0.02	3.00	0.67	0.33	7.50	1.00	0.00	2.50	0.63	0.37
0.05	0.50	0.78	0.22	7.50	1.00	0.00	4.00	0.67	0.33
8-hydroxyquinoline									
0.01	2.50	0.55	0.45	8.50	1.00	0.00	5.00	0.71	0.29
0.02	3.50	0.78	0.22	8.00	0.94	0.06	6.00	0.75	0.25
0.05	4.00	0.89	0.11	7.00	0.82	0.18	6.00	0.75	0.25
EDTA									
0.01	3.00	1.00	0.00	7.50	0.88	0.12	4.00	0.67	0.33
0.02	2.50	0.83	0.17	8.00	0.94	0.06	5.00	0.83	0.17
0.05	2.50	0.83	0.17	8.00	0.94	0.06	4.50	0.75	0.25

is such that a major portion of it remains unextracted in acid ammonium oxalate i.e. larger fraction is in fixed form.

Various complexants added to soils have variable effect in increasing E/R ratios. However, a fivefold increase in the concentration of added complexants does not appear to affect E/R values proportionately. Ammonium oxalate and EDTA appear to affect E/R to a maximum extent leading to increased values. The increases are 4-37, 11-28 and 0-38 per cent in black, red and alkali soils respectively. The red and alkali soils are quite similar with respect to complexants in increasing E/R values. But to black soil behaves in two different ways, viz. it gives increased E/R values with ammonium oxalate, sodium salicylate, 8-hydroxyquinoline and EDTA but decreased values with potassium thiocyanate and aluminon.

Though it is very difficult to explain the mechanism by which complexants affect the molybdenum-supplying power of soils, yet, at least, this much can be said that the red soil further improves E/R in which the values are very high and hence the chances for the conversion

of added molybdenum to fixed forms are greatly minimized. This appears to be an important effect of complexants.

The decreased E/R values in black soil in presence of potassium thiocyanate and aluminon further point to a need for a proper understanding of the fate of complexants in formulating the chemistry of molybdenum added to soils under water-logged conditions. The little molybdenum that is available in soils initially may further be decreased by the presence of potassium thiocyanate and aluminon.

Acknowledgement

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Differential thermal analysis of some urea-form fertilizers having U/F ratios ranging from 0.8:1 to 1.8:1 has been made with a view to characterize the products formed by condensation of urea with formaldehyde at pH—4 and room temperature. It has been observed that constituents, like methylene diurea, dimethylene triurea and possibly one polymethylene urea compound having melting points 205-215, 260-265 and 320°C respectively, are formed in these samples as a result of condensation. When the U/F ratio is more than 0.8:1 free urea is always present in them. Furthermore, except the polymethylene-urea compound, the constituents of the urea-form fertilizers decompose at their melting temperature.

Characterization of Urea-Form Fertilizers by Differential Thermal Analysis

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Introduction

Urea-form compounds prepared by condensation of urea with formaldehyde has been found to be a very useful fertilizer for long season crops. Such products under acidic conditions normally comprise of polymethylene ureas and free urea¹⁻³. X-ray diffraction study has been utilized to identify the crystalline components in the urea-form fertilizers^{4,5} and compounds, like dimethylene triurea (NHCONH)(NH₂CONH)₂(CH₂)₂ and methylene diurea (NH₂CONH)₂CH₂, have been identified in them when prepared with molecular ratios of urea to formaldehyde (U/F) 1.5:1 to 2.0:1 at pH—4 and room temperature.^{4,5} But those components, which are amorphous and likely to be formed as a result of condensation, cannot be identified by x-ray diffraction study. Differential thermal analysis (DTA) has been utilized successfully for identification of such compounds; moreover, it offers unique advantages over other instrumental analyses, especially those involving insoluble colloidal and amorphous aggregates, which exhibit diffused x-ray patterns and which, because of their inherent interactable physical state, do not give reproducible infrared spectra⁶. Although attempts have been made to characterize different organic substances and polymers by DTA^{6,7} yet there is no available

information in the case of urea-form condensation products.

Considering this, an attempt has been made in the present investigation to characterize the urea-form fertilizers prepared by condensation of urea with formaldehyde in different molecular ratios by differential thermal analysis.

Experimental

Urea-form fertilizers were prepared by condensing of urea with formaldehyde at pH—4 and room temperature⁴. The condensation products having U/F ratios of 0.8:1, 1:1, 1.3:1, 1.6:1 and 1.8:1 were taken for this present investigation. Also A.R. grade urea was taken along with these samples for comparison of their thermograms with that of urea.

Differential thermal analysis (Fig. 1) of these samples was carried out in a manually operated apparatus fabricated in this laboratory using nitrogen atmosphere. The temperature range was 24 to 600°C and the rise of temperature was maintained at 10°C/min. The thermo-

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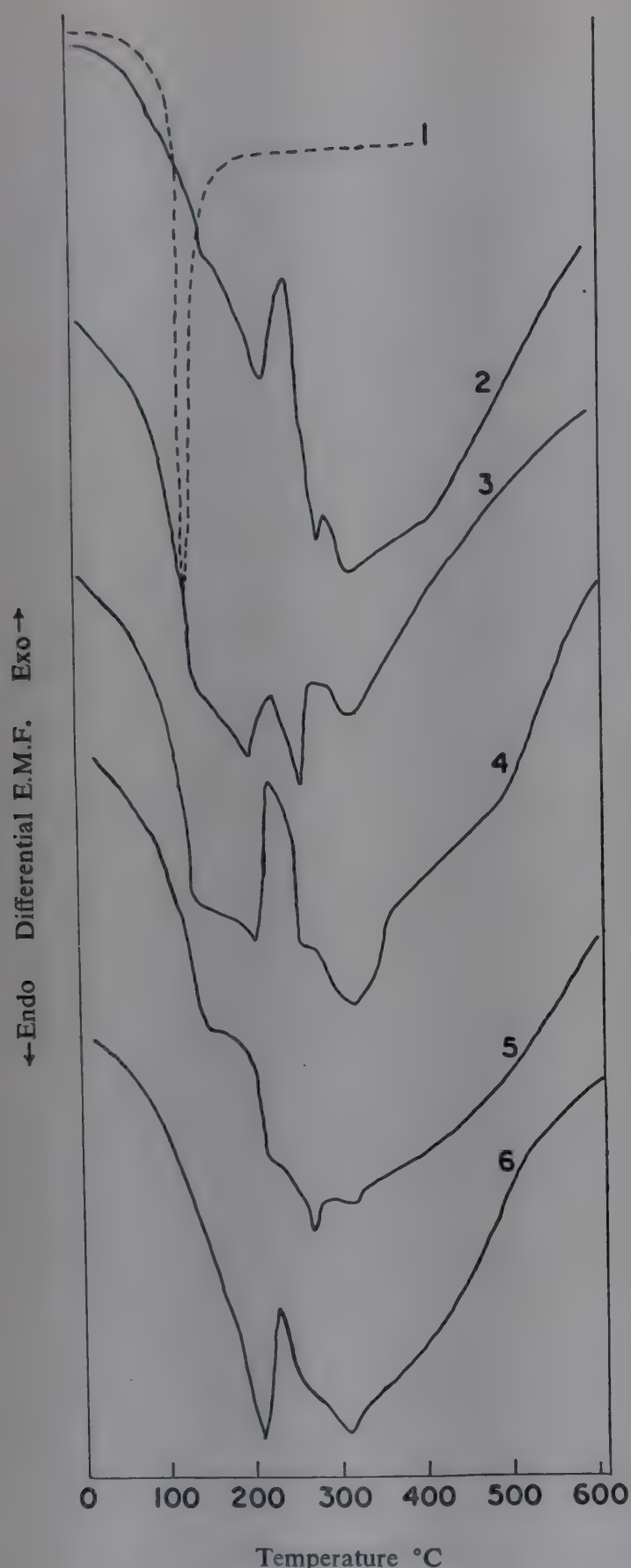


Fig. 1—DTA Thermograms of Urea-form Fertilizers

LEGEND

1. Urea
2. U/F=1.8:1
3. U/F=1.6:1
4. U/F=1.3:1
5. U/F=1.0:1
6. U/F=0.8:1

couples for temperature measurement as well as the differential e.m.f. were of chromel/alume composition. The sample holders were made of thin platinum cylinders

and the reference substance was $\alpha\text{-Al}_2\text{O}_3$. The results are given in Table 1.

Thermogravimetric analysis (TGA) of one sample having U/F ratio 1.8:1 was performed in ordinary atmosphere. The derivative of TGA (DTGA) was plotted (Fig. 2).

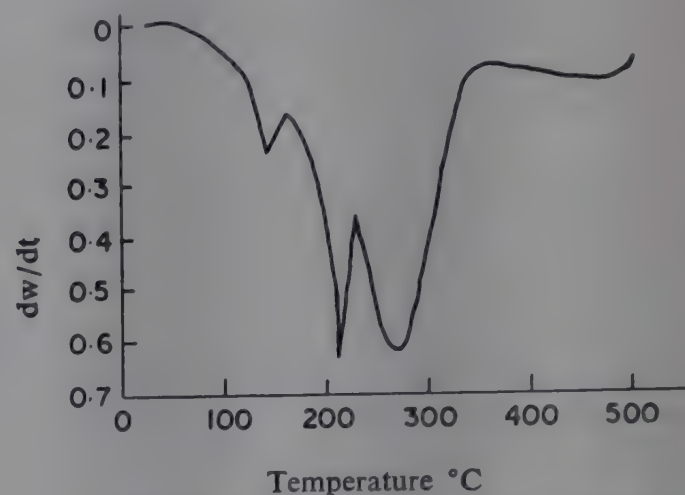


Fig. 2—Derivative Thermogravimetric Analysis of Urea-form (U/F 1.8:1) Fertilizer

TABLE 1—PEAK TEMPERATURE AND INTENSITY OF UREA-FORM SAMPLES

Peak Temperature, °C	
Sample U:F.	Endothermic
0.8:1	210 s
	260 wb
	320 s
1:1	150 wb
	215 wb
	260 wm
	320 w
1.3:1	135 wb
	205 m
	260 w
	320 s
1.6:1	140 wb
	205 s
	265 s
	320 m
1.8:1	150 wb
	215 s
	260 w
1.0:1	320 m
	130 s

s-strong, m-medium, w-weak, b-bulge.

Results and Discussions

It is evident from the thermograms of the urea-formaldehyde condensation products that they show three distinct endothermic peaks at 205-215, 260-265 and 320°C (Fig. 1, Table 1). There is also one weak endothermic bulge that appears at 135-150°C in the thermograms of all the samples except that having U/F ratio 0.8:1. This peak is very similar to that of urea which is observed in its thermogram (Fig. 1). In the case of urea, this peak originates from its melting and decomposition. Its appearance in the urea-form fertilizers is, therefore, due to melting and decomposition of free urea, which is present in the samples. The other phases identified are methylenediurea and dimethylene triurea^{4,5}, having higher U/F ratios. Their melting points have been found to be 213 and 270°C respectively⁸. Therefore, the appearance of endothermic peaks at about 210 and 260°C is due to melting of methylene diurea and dimethylene triurea respectively. From the DTA results (Fig. 1, Table 1), it is, thus, evident that both the constituents are formed in the urea-formaldehyde condensation products whose U/F ratios varying from 0.8:1 to 1.8:1. Further, the appearance of the endo-thermic peak at 320°C may indicate melting of another compound—possibly a member of the polymethylene ureas—which has not been identified so far. This unidentified compound is also formed as a result of condensation of urea with formaldehyde.

In order to verify whether these constituents decompose on heating in air, the derivative thermogravimetric analysis (DTGA) of one of these condensation products (U/F 1.8:1) has been performed. In the DTGA thermogram (Fig. 2), distinct peaks at 140, 210 and 270°C are formed, which are evidently due to decomposition of urea, methylene diurea and dimethylene triurea respectively. From this result, it may therefore be inferred that these methylene ureas decompose simultaneously on melting. But no peak at 320°C is observed in the DTGA thermogram. This indicates that the unidentified polymethylene urea compound does not decompose at melting temperature.

Acknowledgement

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The mechanism of interference on calcium by orthophosphate and pyrophosphate has been studied. Calcium—orthophosphate and pyrophosphate solutions have been aspirated and collected over hot glass slide with the flame off and the unevaporated portion of calcium—orthophosphate system was collected over the flame. X-ray diffraction pattern reveals that the initial products in cases of orthophosphate and pyrophosphate are calcium hydrogen phosphate (CaHPO_4) and acid calcium chloride phosphate hydrate [$\text{CaCl}_2 \cdot \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$] respectively. In the unevaporated portion of orthophosphate only calcium pyrophosphate is detected. A reaction mechanism of interference has been suggested.

Phosphate Interference on Calcium in Flame Spectrometry

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The effect of the interfering ions on analytical signal of the alkaline-earth elements in the flame is always of interest for study to the flame spectroscopist. Phosphate, silicate, aluminium and sulphate depresses the absorption of calcium in the conventional flames. Among these, phosphate interference is severe and has been studied extensively¹⁻¹³. It has been observed that orthophosphate as well as pyrophosphate depress calcium upto the point where calcium to orthophosphate and pyrophosphate mole ratios are 3:2 and 1:1 respectively. It has been further investigated by Smith and Winefordner¹⁰ that the degree of interference decreases with the height of observation in the flame. It has also been observed by them that when both phosphate ions are in excess than in the stoichiometric ratio, the depression in the signal for orthophosphate as well as pyrophosphate, is the same in oxy-hydrogen turbulent flame.

Two theories have been put forward to explain the interference due to phosphate ions. The first theory^{1,2,12,13} is based on the formation of refractory compounds which do not decompose completely in the flame. Smith and Winefordner¹⁰ supporting this theory explain that the depression in calcium signal by orthophosphate and pyrophosphate is due to slow dissociation of their respective calcium salts. The second theory, based on the study of Pungor³ and supported by the observation of Yafee et al,^{5,6} attribute the interference due to gas-phase reaction. In the case of calcium-orthophosphate system, calcium orthophosphate

first converts to more refractory pyrophosphate and calcium oxide. The depression in the signal is due to slow dissociation of this pyrophosphate. In case of pyrophosphate system also the depression is due to slow dissociation of calcium pyrophosphate.

In the present study the mechanism of interference of orthophosphate and pyrophosphate ions on calcium in acidic solution has been investigated. The solution of calcium with orthophosphate and pyrophosphate has been aspirated and collected over the hot glass slide, with the flame off. The components collected over the hot glass slide after evaporation of aerosol can be well considered as the product in the initial stage of the flame. The unevaporated portion of calcium orthophosphate system was collected over the flame on fused quartz crucible. Rubeska and Moldan⁸ made the similar study by collecting the unevaporated portion over the study by collecting the unevaporated portion over the flame to explain the interference mechanism of aluminium on magnesium and calcium.

Sample Preparation and Procedure

A solution was made by mixing 2,000 ppm of calcium, prepared from the calcium carbonate (AR) with a minimum amount of hydrochloric acid and 2,000 ppm phosphorous as orthophosphoric acid. Another solution of 0.5 per cent calcium pyrophosphate with minimum amount of hydrochloric acid was prepared. Calcium

pyrophosphate was made by reacting calcium chloride and sodium pyrophosphate in alkaline medium.

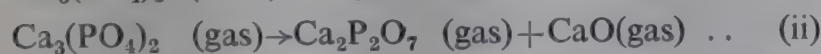
The above solutions were aspirated through the Perkin-Elmer standard premix acetylene burner assembly and collected on the hot glass slide with the flame off. The air at 30 psi was used for the aspiration of the samples. These dried samples were scraped and filled in Lindemann glass capillary and mounted on the Debye-Sherrer 11.46 cm. diam. camera. The source used was $\text{CuK}\alpha$ radiation with nickel filter and the time of exposure 5 hr. for each sample.

The calcium chloride phosphoric acid solution was aspirated in the air-coal gas flame. The coal gas burner used was of Lunge's standard model (Mecker burner) and the unevaporated portion was collected on the smooth fused quartz basin for $3\frac{1}{2}$ hr. A few drops of collodion was added and the paste was rolled into a rod-shaped specimen in collodion. The x-ray diffraction pattern was taken as above.

Results & Discussion

Calcium-Orthophosphate System: In the present study diffraction pattern of calcium orthophosphate system reveals that the calcium hydrogenphosphate was the principal phase in the sample collected with the flame off. The other, very minor, phase could not be properly identified. This is not in agreement with the computerized data of Perrin and Sayce¹⁴, which suggests the absence of calcium hydrophosphate (CaHPO_4) in acidic medium. In the unevaporated portion of the above sample in the flame showed presence of calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$).

The earlier theory,^{1,2,12,13} which is recently supported by Smith and Winefordner¹⁰, proposed that in calcium-orthophosphate system calcium orthophosphate slowly decomposes in the flame. The second theory, based on Pungor's¹³ observation and supported by Yafee et al.,^{5,6} suggests the following gas-phase reaction (equations i and ii).



According to the present x-ray diffraction investigation, the reaction suggested by Pungor³ is more probable but the intermediate reaction is different. The probable reaction is as follows:

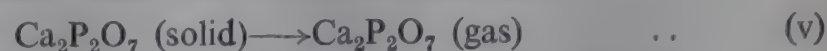


The ultimate product is pyrophosphate. This is not in agreement with the earlier theory¹⁰. The absence of

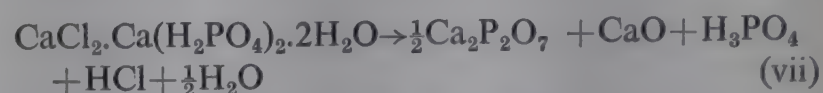
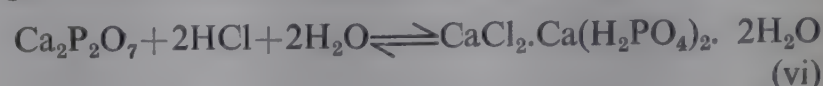
CaO lines in diffraction pattern may be due to excess of phosphoric acid.

Calcium-Pyrophosphate System: In x-ray diffraction studies of calcium-pyrophosphate system, it was found that the aspirated sample, when collected on the hot slide with the flame off, is acid calcium chloride phosphate hydrate $[\text{CaCl}_2 \cdot \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}]$.

The reaction mechanism of pyrophosphate interference by the earlier theory, which has been supported by Smith and Winefordner,¹⁰ suggests slow decomposition of calcium pyrophosphate, while according to Pungor³ it first gets converted to gas phase, as shown below and then slowly dissociates.



But the present x-ray results can be interpreted according to the following reaction in the acidic medium.



A part of $\text{CaCl}_2 \cdot \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ may directly convert into pyrophosphate (equation vi) and another part may convert to pyrophosphate and calcium oxide in the flame. Smith and Winefordner¹⁰ compared the depression of orthophosphate and pyrophosphate on calcium and rightly concluded that according to Pungor's theory in case of orthophosphate (equation iii), the depression should be less as CaO will contribute substantially for the enhancement of atomic calcium signal but this enhancement was not observed experimentally; both the ions exhibited equal interference¹⁰, when their concentration is in excess of the stoichiometric ratio.

The present investigation does not prove the equality of depression for the ortho-phosphate (equation i) as well as for pyrophosphate (equation vi & vii), but it is expected that the depression is of the same order in magnitude. This difference, with the experimental observation may be due to the droplet size and different burner design. In case of chamber type premix air-acetylene flame, Smith and Winefordner¹⁰ did not observe the interference in low calcium concentration. At higher concentration the interference for both the phosphate ions, when in excess, was also not found equal. They attribute this difference to the drop size variation in premix, chamber-type burner. Further investigations on this subject are in progress.

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Investigation on the material of construction and corrosion products by x-ray, thermomagnetic and metallography techniques has revealed that the failure of AISI-304 type stainless steel heat exchanger tubes was due to sulphide corrosion cracking.

Sulphide Corrosion Cracking in Stainless Steel Tubes

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Leakages were observed in a few tubes of CO-conversion heat exchanger of a urea plant*. On taking out the tubes many cracks in a circumferential pattern were observed on the outer surfaces. The inner and outer sides of the tubes were found to be thinly coated with black and brownish-black deposits respectively. Two tubes, viz. one cracked and the other in a good condition, were taken for parallel studies to ascertain the causes of failure. X-ray diffraction, thermomagnetic and metallographic techniques were used for the above purpose.

The heat-exchanger carries converter feed gas through its shell side and converter product gas through its tube side. The gas composition and other process conditions are shown in Table 1. The material of construction as

supplied by the manufacturer was SUS 27 (Japanese), almost equivalent to s.s AISI 304-type. A steeloscopic analysis confirmed the above specification.

TABLE 1—COMPOSITION AND PROCESS CONDITIONS IN THE
CO-CONVERSION HEAT EXCHANGER AS PER DESIGN

Gas	Shell-side	Tube-side
(N ₂ +A), %	1.5	1.4
H ₂ , %	47.7	62.6
CO, %	45.0	2.8
CO ₂ , %	5.4	33.6
CH ₄ , %	0.4	0.6
H ₂ S, ppm	100	83
Steam	SVP	SVP
Max. operating temperature, °C	240	350

*FCI Ltd., Gorakhpur, U.P.

The x-ray diffraction photograph of the bulk material showed the presence of only γ -Fe phase. The scrapings from the outer as well as inner sides of the tubes revealed the existence of magnetite (Fe_3O_4) as the major phase and troilite (FeS) as minor phase. The x-ray diffraction photographs of the troilite shown from the scrapings from both the sides differed slightly in finer details; the structurally disordered form was shown by the scrapings from the inner side, while the pattern of FeS from the outer side showed the tendency of formation of ordered form from the disordered one. This phenomenon may be due to the difference in the temperatures at which

these were formed (Table 2). All the above results were same for leaky and non-leaky tubes.

The thermomagnetic curves of the bulk material showed the typical austenitic structure. The same from the scrapings showed a Curie point at 575°C due to magnetite. But a peculiar phenomenon was observed in the thermomagnetic curves of the scrapings. The magnetic pull at room temperature increased after heating the sample above 575°C . This was difficult to explain (Fig. 1). Later on, this was interpreted as due to the transformation of the diamagnetic phase, FeS , to ferro-magnetic phase, Fe_3O_4 , which gave an enhanced

TABLE 2—X-RAY DIFFRACTION DATA

Bulk Material		γ -Fe ASTM 5-0717		Specimen from Inside Surface		Iron Sulphide ASTM, 1-1247		Magnetite ASTM, 11-614		Specimen from Outside Surface		Iron Sulphide Ordered ASTM, 4-0832	
d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁	d(Å)	I/I ₁
2.093	s	2.08	100	4.81	vw			4.85	40	4.84	vvw		
1.818	w	1.80	80							4.41	vvw		
1.277	w	1.270	50	2.971	m	2.97	33	2.966	70	2.978	m	2.98	90
1.09	ms	1.083	80			2.88	4			2.902	vvw	2.93	50
1.042	vw	1.037	50	2.65	vw	2.65	33			2.653	w	2.67	90
				2.535	vs			2.530	100	2.534	s		
										2.483	vvw	2.52	30
				2.425	vw			2.419	10	2.429	vvw		
												2.15	50
												2.14	50
				2.101	m			2.096	70	2.09	ms	2.09	100
				2.075	w	2.06	100			1.932	vvw	1.95	50
												1.92	60
												1.75	60
				1.715	w	1.71	33	1.712	60	1.728	w	1.72	90
												1.64	60
				1.618	ms	1.61	7	1.614	85	1.618	w	1.62	40
												1.60	40
												1.50	50
				1.487	s	1.48	4	1.483	85	1.489	m	1.49	50
												1.47	60
												1.46	50
				1.44	vvw	1.44	9			1.448	vvw	1.44	60
												1.42	50
												1.34	40
				1.327	vw	1.32	13	1.327	20	1.335	vw	1.33	80
												1.32	50
				1.281	w	1.30	5	1.279	30	1.283	vw	1.28	40
				1.267	vvw			1.264	10	1.267	vvw	1.27	40
				1.213	vw			1.2112	20	1.217	vvw	1.23	40
												1.19	40
				1.172	vvw	1.18	1			1.178	vvw	1.18	40
				1.122	w			1.1214	30	1.123	vvw		
				1.107	vvw	1.11	13			1.109	vvw		
				1.095	ms			1.0922	60	1.096	vw		

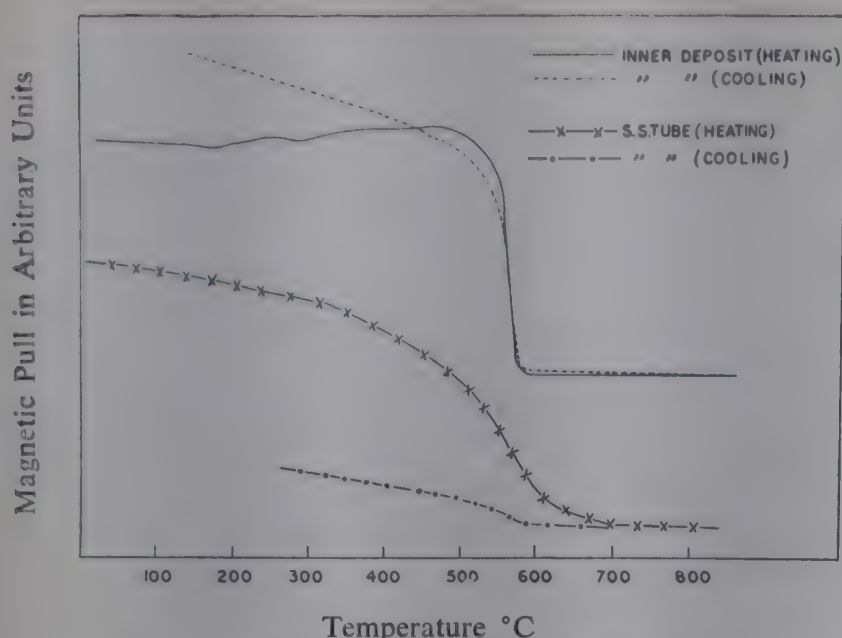


Fig. 1—Thermomagnetic Curves of Scrapings & S. S. Tube

magnetic pull below the Curie point. These results were also same for the leaky and non-leaky tubes.

A metallographic analysis of the non-leaky tube showed that the material had a normal austenitic structure. But the leaky tube revealed predominantly transgranular type of cracking in an austenitic structure (Fig. 2).

The gas analysis (Table 1) show that there were small amounts of hydrogen sulphide—about 100 ppm in the



Fig. 2—Micrograph of Leaky Tube $\times 500$

shell-side and about 83 ppm in the tube-side. Though little, this amount of hydrogen sulphide in presence of steam produces, as shown by x-ray and thermomagnetic analyses, iron sulphide scales, which get further oxidized and hydrolysed to form polythionic acid¹. The cumulative effect of this process, in the long run, results in sulphide corrosion cracking.

The type of cracking in polythionic acid environment depends on the thermal history of the stainless steel. It has been found that sensitized austenitic steels crack through grain boundaries and annealed specimens crack across the grains². Evidence of predominantly transgranular type of cracking (Fig. 2) indicate that this is a case of cracking of the annealed tubes. Full annealing would have been done at the fabrication shop for its improved physical properties and/or incomplete annealing for stress-relieving at the welded joints of the tubes with the shell plate.

Thus, from this investigation, the cracking and leaking of AISI 304 type stainless steel in the heat exchanger of CO-conversion unit appears to be mainly due to the presence of hydrogen sulphide in the process gases. To minimize this sort of failure, it is recommended to use thermally stabilized stainless steels around 871-899°C for 4 hours, as these are found more resistant to polythionic acid attack¹. The chemically stabilized AISI 316, 321 or 347 stainless steels, further stabilized thermally under the above conditions,^{2,3} may offer a better solution. The flushing of the tube and shell sides with nitrogen or highly alkaline water during shut-down for neutralizing the polythionic acid may also reduce the tendency to corrosion-cracking. The best remedy, however, lies in eliminating hydrogen sulphide completely from the process gases.

Acknowledgement

The authors' thanks are due to Dr. B. K. Banerjee, Addl. Supdt. (PRW), and Sri K. C. Banerjee, Dy. Supdt. (PRW), for their interest in the work. Thanks are also due to Sri R. C. P. Sinha, Technologist (PRW), for carrying out the steeloscopic analysis.

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the addition of ammonium sulphate to ammonium nitrate and calcium ammonium nitrate greatly influences the behaviour of the final products towards $IV \rightleftharpoons III$ phase change of ammonium nitrate. With increasing amounts of ammonium sulphate, although the transition temperature is not much affected, the transition damage is reduced considerably. Products containing 35 per cent and above by weight of ammonium sulphate do not undergo transition because of the formation of double salts which have different crystal structures than that of ammonium nitrate.

Influence of Ammonium Sulphate on the Phase Transition of Ammonium Nitrate and Calcium Ammonium Nitrate Granules

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In an earlier communication¹, the influence of ammonium sulphate on ammonium nitrate and CAN was studied with particular reference to their transition-damage. It was observed that the transition temperature of the phase change $IV \rightleftharpoons III$ in ammonium nitrate is not affected by the addition of 2 per cent ammonium sulphate. It, however, increased the stability of the ammonium nitrate towards the temperature fluctuations involving transition temperature.

It has been observed that the ammonium sulphate-nitrate produced at Sindri does not undergo phase transition on heating between 20° and 50°C. Thus, there is absolutely no volume-increase. The same observation has been made in the case of laboratory-prepared samples, containing ammonium sulphate and ammonium nitrate in 1:1, 1:2 and 1:3 mole ratios. In the present communication, the influence of various concentrations of ammonium sulphate added to ammonium nitrate and CAN towards phase transition and hence the extent of transition-damage have been reported, which has indicated that the ammonium sulphate added influences to a great extent the behaviour of the final product towards transition-damage of the granules. The preparation of the samples was carried out, as reported earlier¹, by dissolving the requisite amount of ammonium nitrate in water followed by addition of ammonium sulphate. The solution was evaporated on a

water-bath till a pasty mass was obtained, which was then transferred to a paddle-type granulator and the granules obtained were sieved to the required size (−5,+8 B.S.S.). The granules were dried over sulphuric acid and then the desired amount of moisture allowed to be absorbed by the granules. The samples were immediately used for experimentation to avoid possible changes in moisture and temperature.

In the case of CAN samples, chalk was added after the dissolution of the ammonium nitrate and ammonium sulphate and before evaporation on the water-bath. The measurement of the transition temperature was carried out, as reported earlier,¹ involving a dilatometric technique using turpentine oil as the dilatometric liquid. Similarly, the increase in volume of the sample for every temperature cycle involving the transition temperature was measured as reported in the earlier communication.

Results & Discussion

In Table 1 are presented the transition temperatures as well as the number of temperature cycles which the product containing varying amounts of ammonium sulphate undergoes before final disintegration, whereas in Fig. 1 the amount of ammonium sulphate added to the sample has been plotted against the total number of temperature cycles for complete disintegration of the

TABLE 1—TRANSITION TEMPERATURE AND THE NUMBER OF TEMPERATURE CYCLES FOR DISINTEGRATION OF AMMONIUM NITRATE CONTAINING AMMONIUM SULPHATE

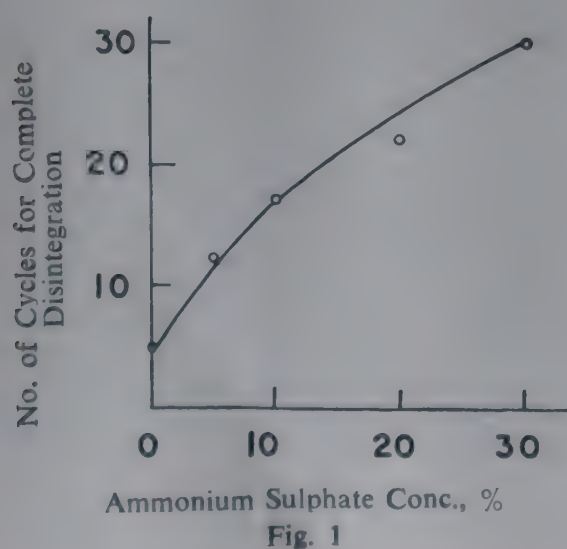
Ammonium Sulphate, % by wt.	Transition Temp., °C	No. of Cycles for Complete Disintegration
2	37	10
5	38	12
10	38	17
20	38	2
30	38.5	31
35*	No expansion	—
45*	do	—
Double Salt from Sindri Plant	do	

*35 and 45% by wt. of ammonium sulphate in ammonium nitrate correspond to the formation of 1:3 and 1:2 double salts respectively.

product. As can be observed, the transition-damage is reduced by increasing the amount of ammonium sulphate, which has considerable influence on the final disintegration of ammonium nitrate as well as CAN.

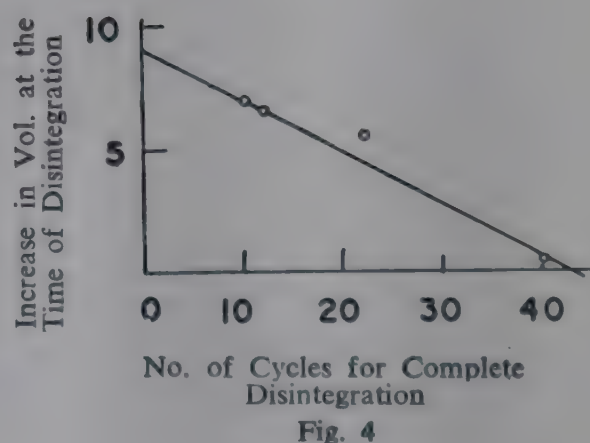
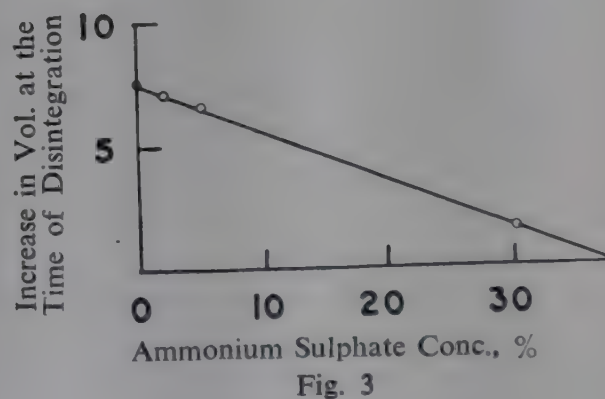
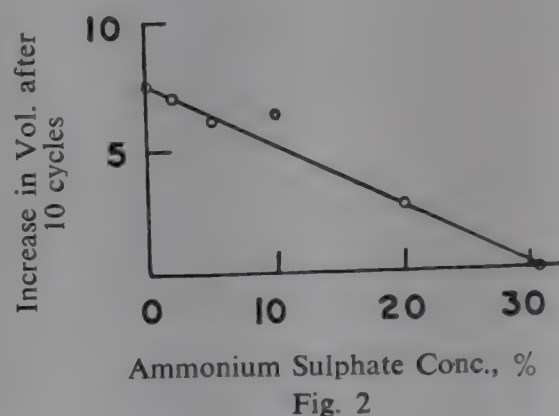
The other factor studied in details was the increase in volume accompanying each phase transition. As reported earlier, the volumes of ammonium nitrate and CAN go on increasing with each heating cycle passing through the transition temperature. In Fig. 2 the increase in volume after 10 cycles of various samples of ammonium nitrate containing ammonium sulphate has been plotted against the concentration of ammonium sulphate. The plot shows clearly that the increasing amounts of ammonium sulphate tend to lower the slope of the plot which ultimately falls to zero at about 35 per cent ammonium sulphate concentration.

Ammonium sulphate concentration as well as the number of cycles for complete disintegration have been



plotted individually against the increase in volume at the time of disintegration in Figs. 3 and 4 respectively. Both these curves indicate that the increasing volumes of ammonium sulphate reduce considerably the expansion of the fertilizer samples, thus helping in the improvement of the storage behaviour of the fertilizers.

The data presented above indicate that although the temperature of transition of ammonium nitrate has not been found to be much influenced by the presence of ammonium sulphate, the stability of the granule does increase with the increasing concentration of ammonium sulphate. With progressive increase in the concentration of ammonium sulphate, it was found that when it reaches 35 per cent by weight of the final product, the transition disappears. It is significant to note in this connection that this concentration of ammonium sulphate corresponds to the double salt $(\text{NH}_4)_2\text{SO}_4 \cdot 3\text{NH}_4\text{NO}_3$. Thus,



probably, the formation of this double salt involves change in the crystal structure of the final product, which is different from that of pure ammonium nitrate and thus does not undergo any transition on heating. X-ray studies have also revealed that the double salt formed between ammonium sulphate and ammonium nitrate has a crystal structure different than that of pure ammonium nitrate². The differential thermal analysis of the recrystallized product of ammonium nitrate and ammonium sulphate in the ratio 3:1 also indicates the absence of the peak due to phase IV $\rightleftharpoons$ III transition³, which is shown in the case of pure ammonium nitrate.

On increasing further the concentration of ammonium sulphate upto 65 per cent by weight corresponding to 1:1 double salt, there was no specific change in the behaviour of the sample towards volume-change when subjected to temperature cycles between 20° and 50°C.

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Suitability of a coal tar-based wash oil prepared in the tar distillation plant at Sindri for scrubbing light oil from enriched coke oven gas has been investigated. On the basis of the study made in the laboratory as well as during use in the gas stream of coke-ovens plant, it has been found that the oil has a desirable specific gravity, low viscosity, a moderately high boiling range, low emulsification tendency with water, high light oil absorptive capacity and negligible insoluble sludge formation, etc., indicating that it is highly suitable for efficient light oil scrubbing.

The relative merits and demerits of its use compared to those of petroleum-based wash oils have also been discussed.

Studies on the Scrubbing of Light Oil from Coke Oven Gas by Liquid Absorbents Part II: Coal Tar Wash Oil

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Introduction

In the by-product coke-oven plants, a suitable wash oil derived from either petroleum or coal tar is widely used as an absorbent for light oil scrubbing from the enriched coke-oven gases¹⁻³. Among these oils the coal tar-based wash oils have been more widely used since such an oil could be easily produced from the indigenously available coal tar in the plant itself. In an

earlier communication⁴, data on the characteristics and evaluation of some petroleum-based oil fractions, for the light oil scrubbing, were reported. In this note, a coal tar-based wash oil prepared in the tar distillation plant at Sindri, has been investigated for its suitability in scrubbing light oil from enriched coke oven gas, and its characteristics as determined in the laboratory as well as observed during its use in the gas stream

of Sindri factory's coke ovens plant are discussed. Besides these, the relative merits and demerits of its use for the light oil scrubbing compared to petroleum-based wash oils have also been discussed.

Experimental

Materials Used: The investigation was carried out on the wash oil produced in the tar distillation plant of this Division. The wash oil was prepared by distilling a high temperature coal tar (Table 1), produced at Sindri factory's coke ovens plant, batchwise in a suitable still. The different distillates boiling in the range 230-310°C were collected and suitably processed for removal of undesirable ingredients, like naphthalene, anthracene, etc. Finally, a suitable blend of these processed coal tar oil fractions was prepared. The suitability of the oil thus produced was investigated for light oil scrubbing from the enriched coke oven gas.

TABLE 1—CHARACTERISTICS OF THE COAL TAR PRODUCED AT SINDRI

Sl. No.	Characteristics	Sindri Coal Tar
1.	Moisture	0.6% w/w
2.	Distillation Range Analysis: Temperature, °C	% of Total distills over by wt.
	Up to 170	1.29
	170-230	6.67
	230-270	10.92
	270-300	4.76
3.	Pitch	75.8
4.	Softening Point of Pitch (R & B)	51.0°C
5.	Viscosity by B.R.T.A. Viscometer (4 mm. cup)	14.5 at 45°C
6.	Phenols	2.18% by wt.
7.	Naphthalene	6.16% by wt.
8.	Matter Insoluble in Toluene	8.2% by wt.
9.	Specific Gravity	1.17 at 25°C.

The light oil (crude benzole) used during the present study was obtained from the coke ovens plant at Sindri.

Procedure

(i) **Characteristics of the Wash Oil:** The characteristics, like specific gravity, specific viscosity (Engler), water content, low boiling oil content, distillation range analysis, phenol content, naphthalene content, emulsification with water, etc., were determined by the appropriate standard methods^{3,5,6}. The values obtained are recorded in Table 2.

TABLE 2—CHARACTERISTICS OF COAL TAR BASED WASH OIL PRODUCED AT SINDRI

Sl. No.	Characteristics	Wash Oil produced in Tar Distillation plant at Sindri	
1.	Specific Gravity at 30°C	1.053	1.055
2.	Specific Viscosity (Engler) at 30°C, °E	1.29	1.30
3.	Water content (% v/v)	0.6	0.5
4.	Benzole content (% v/v)	1.4	1.0
5.	Distillation Range Analysis: Temperature, °C	% of total oil distills over, by vol.	
	Up to 200	4	5
	210	12	11
	220	28	26
	230	41	43
	240	54	56
	250	66	64
	260	74	71
	270	81	76
	280	85	81
	290	88	83
	300	92	88
6.	Phenol content (% v/v)	8.5	9.8
7.	Naphthalene (% W/V)	17	13
8.	Emulsification with water (100 ml. of the Oil shaken vigorously for 30 secs. with 100 ml. of water at 30°C).	Oil/Water Separation was rapid and almost complete in 10 min.	Oil/Water Separation was rapid and almost complete in 10 min.
9.	Foam Formation (On aeration at the rate of 25 c.c./min./20 ml. of the oil at 30°C).	Low	Low

(ii) **Benzole Retention Capacity:** The benzole retention capacity of the wash oils was determined in the same manner as described in the earlier communication⁴. The benzole content of the scrubbed air over the benzolized wash oils is shown in Fig. 1.

(iii) **Sludge Formation in the Wash Oil:** The formation of sludge in the oil on passing enriched coke oven gas through the oil was studied by performing three complete cycles of light oil absorption and regeneration in the same manner as described in the earlier communication⁴. After completion of such three cycles, benzole retention capacity, viscosity of the used oil and the total amount of sludge formed were determined (Fig. 1., Table 3).

Results & Discussion

An examination of the different properties of the two typical samples of the coal tar wash oil (Table 2) indicates

TABLE 3—SLUDGE FORMATION IN COAL TAR BASED WASH OIL PRODUCED AT SINDRI

Cycle No.	Wash Oil	Specific Viscosity (Engler) at 30°C, °E.	Volume of Oil taken, ml.	Volume of Coke Oven Gas passed, l.	Flow Rate of the Gas, l/hr.	Total Amount of Sludge separated Coke in Three Complete Cycles, g.	Amount of Sludge Formed when Coke Oven Gas Passed, g./m ³
1.	Fresh Wash Oil	1.29	200	1000	50	—	—
2.	Used Wash Oil (Once regenerated)		Whole of the debenzolized oil of cycle No. 1.	1000	"	—	—
3.	Used Wash Oil (Twice regenerated)		Whole of the debenzolized oil of cycle No. 2.	1000	"	—	—
4.	Used Wash Oil (Twice regenerated)	1.94	—	—	—	Negligible	Negligible

clearly that the composition of the oil remains very constant when produced under a particular set of conditions. It can be seen that the specific gravity of the wash oils varies within a narrow range, an average figure being 1.054 at 30°C and is considerably different from that of water. This is desirable for a rapid and almost complete separation of the oils from oil-water mixture and to avoid their emulsification in the decanters. The specific viscosity being quite low—normally found 1.30°E at 30°C—the oils are suitable for better distribution and intimate contact with the gas in the conventional counter-current light oil scrubbers besides having low pumping costs.

The distillation range analysis further shows that the oils have a little low boiling oil content and about 90

per cent by volume of the oil distils over at 300°C. Using this oil, the losses due to vaporization during the scrubbing operation as well as in the debenzolization process would be low and consequently the requirement for fresh oil, for periodical make-up purposes would also be low.

The low concentrations of benzole in the scrubbed gas over the benzolized wash oil (Fig. 1) indicate that upto a benzole concentration of about 2.5 g./100 ml. of the oil, the wash oil has a substantially high benzole retention capacity i.e. having a high benzole absorption power. It could also be seen that these oils show a relatively higher benzole absorption capacity compared to petroleum-based wash oil (Fig. 2).

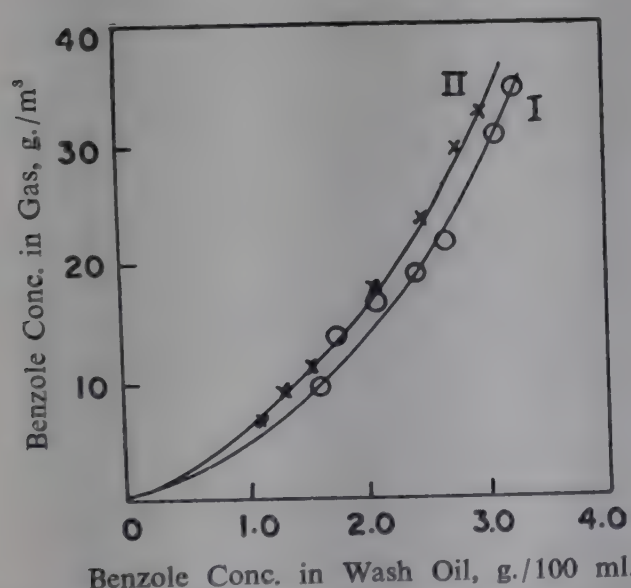


Fig. 1—Variation of Benzole Content in Gas with Change in Benzole Concentration in Benzolized wash Oil

LEGEND

- I—Sindri Coal Tar Wash Oil (Fresh)
- II—Sindri Coal Tar Wash Oil (Used)

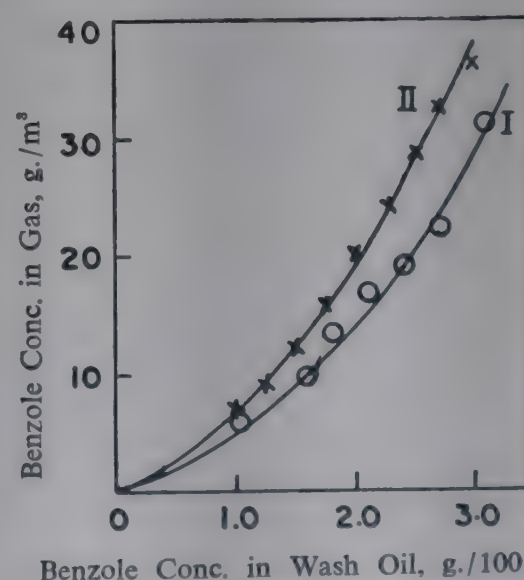


Fig. 2—Comparative Benzole Retention Capacity of Coal Tar and Petroleum-based Wash Oils

LEGEND

- I—Sindri Coal Tar Wash Oil (Fresh)
- II—Petroleum Wash Oil C (Fresh)

The formation of insoluble sludge on passing the enriched coke oven gas through the fresh oil, was practically nil even after completion of three complete cycles of absorption and debenzolization. Also there was no deposition of the sludge on the surfaces of the absorber as well as on the regenerating apparatus. This is possibly due to a high solubility of the tarry matters in the coal tar-based wash oils.

From the characteristics of the used wash oil, it is seen that the viscosity (Table 3) changes on repeated use of the regenerated oil, thereby showing greater tendency to thicken on continuous use. The benzole retention capacity data of the used oil show a slightly lower absorption power compared to the original value (Fig. 1), although the capacity even after repeated use was appreciably high.

A comparative study of the petroleum-based as well as of the coal tar-based wash oils with the point of view of their utilization for light oil scrubbing from the enriched coke oven gas reveals the following facts.

The petroleum-based wash oils possess certain advantageous properties over the coal tar based-wash oils, the important ones being the retention of low viscosity and benzole absorptive capacity of the oils even after its use in repeated cycles of absorption and regeneration, thereby maintaining desirable properties necessary for efficient and smooth scrubbing and stripping operations. The absence of any tar acids and emulsification trouble is also an additional advantage.

However, principal drawback in using these oils is the formation of resinous sticky sludges during the scrubbing and subsequently their deposition during regeneration on the surface of the regenerating apparatus, which is difficult to remove sometimes even by mechanical means. Another disadvantage is that a large quantity of oils is required for the initial charges to be circulated in the scrubber, due to their compara-

tively lower absorption capacity; this leads to more expenses in pumping, heating and cooling, with more steam and power consumption in the process.

Conclusion

The use of coal tar-based wash oils for the light oil scrubbing have certain notable advantages over petroleum-based wash oils. The main advantage is that practically no sludge is formed or separated in the oil during scrubbing and the regeneration operation even when the enriched coke oven gas contains tar, mist, etc. could be easily reconditioned by redistillation only. The tarry matters remain dissolved in the oil and ultimately separated in the pitch column of the light oil recovery plant. The quantity of pitch separated in the pitch column at Sindri is of the order of about 3 tonnes/month which is almost the same amount as that of the resinous sludge calculated to deposit on using petroleum oils. From the present investigations, it could be concluded that unless efficient arrangement for purification of the enriched coke-oven gas from tar mist, fog, etc. by use of a suitable electrostatic detarrer is provided, it is advantageous to use coal tar-based wash oil for light oil scrubbing from the coke oven gas.

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Technical Digests

Converter for Ammonia Synthesis

The basic process of Haber for ammonia synthesis has remained unchanged ever since the first commercial unit was commissioned at Oppau (Germany) 50 years ago by I. G. Farbenindustrie. In this process hydrogen and nitrogen in the ratio 3:1 are passed over a suitable catalyst at high pressure followed by condensation and separation of ammonia and the recycle of unconverted gases. A synthesis converter must meet the following requirements: preheating of the feed mixture to 400-430°C, keeping the catalyst bed temperature close to the optimum conversion profile and shielding the high pressure converter shell from the high temperature in the catalyst basket and exchanger.

Invariably in all converters, the pressure shell is cooled by passage of inlet cold gases in the annular space between the shell and the catalyst basket heat exchanger assembly. Practically all converters are equipped with a bottom heat exchanger, where the hot converted gases exchange heat with cold feed gases. The gases are brought to the initial reaction temperature, either in the heat exchanger itself or in some converters it is achieved by further heat exchange in catalyst cooling tubes embedded in the catalyst bed. The difference in various converter types lies mainly in the means adopted to preheat the gases, in the arrangements for the exothermal heat removal and in keeping the reaction temperature close to the optimum.

Among the widely used converters is the quench converter, which consists of several catalyst layers with arrangement of cooling by injecting cold gas. The recently developed radial converter by Haldor Topsoe is a quench-type converter. In the Fauser-Montecatini type converter also, the catalyst bed is divided into 3-4 stages, the gas temperature rises sharply in packed zones by the heat of formation of ammonia but is then indirectly cooled with boiling water in intermediate spaces.

In tubular converters—TVA and NEC types being the typical among them—the catalyst is either placed in tubes or distributed around them. The nitrogen-hydrogen mixture, which is already partly preheated in the bottom heat exchanger, flows either counter-or co-currently with the reaction gases flowing through the catalyst bed. The bottom heat exchanger is, therefore, comparatively short but the temperature profile of the converter deviates considerably from the optimum.

New Co-Current Type Converter: In a paper* presented at the Seminar on Development and Design of Chemical Equipment held in the Indian Institute of Technology, Madras on June 7-8, 1969, Sri Narinder Nath Tangri described a converter—developed at the Planning & Development Division, FCI Ltd—having an adiabatic section followed by a second section with co-current flow cooling tubes, thus enabling better utilization of high pressure converter volume giving higher space-time yields and offering easier temperature control of the catalyst bed.

In this converter (Fig. 1), circulating gas at 150°C containing 2.1 mol. per cent ammonia enters the converter top, flows through the annular space between the

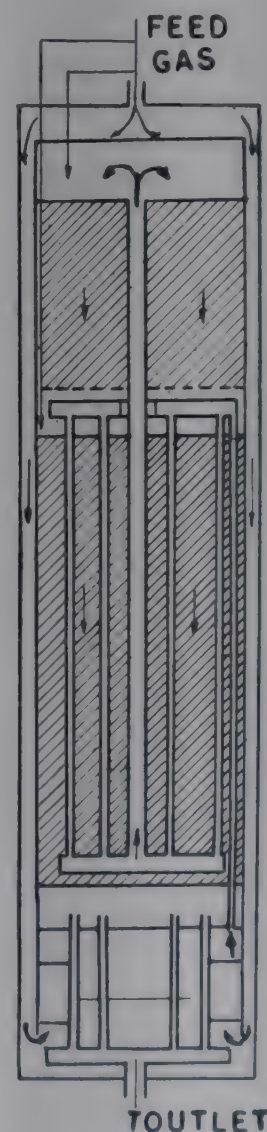


Fig. 1—Co-current flow converter

*A New Co-current Type Converter for Ammonia Synthesis.

catalyst basket and pressure shell and then into the heat recuperator, where gases are preheated upto 250°C at the expense of heat contained in the reacted gases. Subsequently, the gases are led to the catalyst cooling tubes, thereby rising to the reaction temperature (400°C). The cooling surface is so designed that the lower catalyst bed temperature is kept close to the optimum temperature conversion profile.

Leaving the cooling tubes at the bottom, the gases rise through a central pipe where an electric heater for start-up is located and come out above the upper-bed. A stream of cold gas here regulates the entrance temperature. As the gases pass down the upper adiabatic catalyst bed, the temperature and ammonia concentration rise to 523°C and 10.2 per cent respectively. Housing less than 25 per cent of the total catalyst volume, the upper adiabatic catalyst bed contributes more than 50 per cent of ammonia production.

Before the gases enter the lower bed, they meet a cold gas stream for temperature adjustment. The ammonia concentration of the gases leaving the second bed rises to 18 per cent. When properly designed, the co-current cooling system in the lower bed can help maintain the temperature close to the optimum and thus serve as good a purpose as several heat exchangers or quench points incorporated in the catalyst bed.

Further flow of the converted gas into the bottom heat exchanger, waste heat boiler feed gas preheater, water-cooled condenser, separator and the circulation system along with temperature levels at various stages is shown in the flow diagram (Fig. 2). This converter ensures necessary preheating of the gases to the reaction

temperature and effective temperature control of catalyst bed. Owing to reaction temperature remaining close to the optimum, higher ammonia production rates are obtained than with tubular and stage type converters.

From the overall energy balance considerations, it is desirable to recover the reaction heat from synthesis gas converter either by raising steam or by preheating boiler feed water. In this arrangement this heat recovery takes place in a boiler located outside the converter.

Dye for Hydrocarbon Type Analysis

For a quick and accurate determination of aromatic contents of naphtha and kerosene fraction of petroleum products, a fluorescent indicator has been developed using adsorption technique which finds extensive application. Such an indicator method has been recommended by the American Society of Testing Materials (ASTM) and the Institute of Petroleum (London). The technique consists of passing continuously a bulk quantity of the indicator through an adsorption column until the composition of the solution leaving the column is identical with that entering it. The solute molecules are adsorbed preferentially separating the zones. The sharp leading zone is called 'front' and the technique is therefore known as frontal analysis.

The fluorescent indicator or dye has so far been manufactured by Messrs Patent & Chemicals N.J. (USA) from crude oil and its composition is not known. This dye has now been prepared in this laboratory* from indigenous materials and factory wastes and the know-how has been well-established. It has been tested extensively for the representative samples constituting light run distillates, like straight-run naphtha.

Preparation of the Dye: The starting material—high temperature carbonization tar oil in the range 270-310°C—is fractionated on alumina adsorbent by the frontal analysis in the chromatographic column comprising 2 parts—A (600-670 mm. length) and B(300-350 mm.)—of 20 and 10 mm. internal diameter respectively joined together with a tapering column (50-60 mm. length). The yellow fraction of the dye absorbed on the column is eluted with isopropanol and a fraction having refractive index 1.6032—1.6035 at 25°C is collected. This is mixed with red colouring matter and the mixture is adsorbed on silica gel, which is used in the FTA method of analysis for aromatics (ASTM or IP).

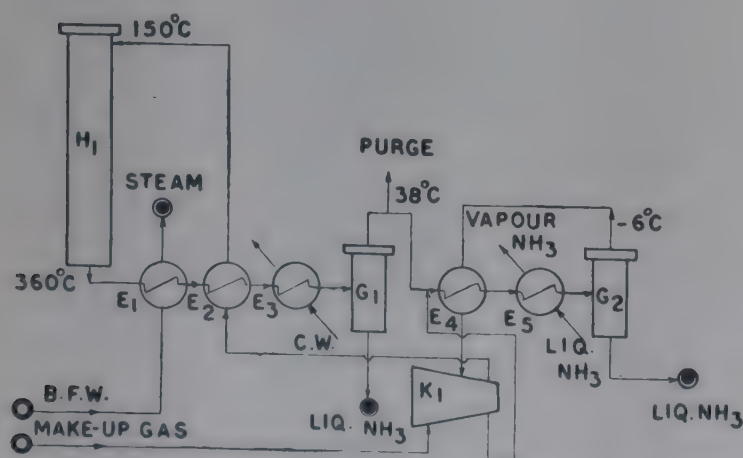


Fig. 2—Flowsheets for Ammonia Synthesis Loop

LEGEND

E ₁ —Waste Heat Boiler	G ₂ —2nd Ammonia Separator
E ₂ —Feed Gas Heater	H ₁ —Ammonia Converter
E ₃ —Water-cooled Condenser	K ₁ —Synthesis Gas Compressor and Recirculator
E ₄ —Cold Gas Exchanger	BFW—Boiler Feed Water
E ₅ —Ammonia Evaporator	C.W.—Cooling Water
G ₁ —1st Ammonia Separator	

*A Process for Preparation of Fluorescent Dye for Hydrocarbon Type Analysis. Indian Patent No. 111101 (Inventors: R. N. Shukla, A. Sinha & K. R. Chakravorty)

Notes & News

New Ammonia Route

For the synthesis of ammonia, the essential details of Haber's process have changed little even today. High temperatures (about 900°F) and high pressures (150-350 atm.) are still needed to induce nitrogen and hydrogen to combine. However, findings at Stanford University (USA) hold promise of a process in which the reaction steps take place at room temperature and pressure. Dr. van Tamelen and co-workers, after examining the nitrogen-fixing properties of such compounds as titanium diisopropoxide and dicyclopentadienyl titanium, which act like catalysts in the sense that they take part repeatedly in a continuous nitrogen fixation-reduction experiment involving other forms of titanium and alternate transition elements that have not been too successful because molecules with nitrogen ligands once made cannot be reduced to ammonia concluded the possibility of arriving at new routes to nitrogen containing compounds.

In a typical experiment, titanium tetraisopropoxide is mixed with a reducing agent, such as naphthalide, in tetrahydrofuran or diglyme. The reactants at room temperature, are stirred under a blanket of nitrogen at atmospheric pressure. The sodium naphthalide reduces the tetravalent titanium compound to the divalent form. Each molecule of the resulting titanium diisopropoxide then binds a molecule of nitrogen. Additional sodium naphthalide reduces this nitrogen complex to the ammonia level. Subsequent hydrolysis (brought about by isopropyl alcohol added to the reaction mixture) yields ammonia. Co-product titanium isopropoxide goes through a repeat of the reaction sequence.

Also unusual is the finding that the nitrogen complex can abstract hydrogen from a normally inert chemical, such as ether, if isopropyl alcohol or similar hydrogen source is lacking.

[*Chem. & Engng News*, 47 (13) (1969), 48]

Pipeline Transport of Ammonia

The present methods of transport of ammonia are by tank trucks, rail cars and barges, of which transport by barges is the

cheapest. But all consumer centres cannot be reached by barge alone and therefore in majority of cases it is combined with an alternate type of transport. This combined method costs a considerable amount. During the last three years long distant transport by pipelines has been seriously considered by many countries.

The world's first ammonia pipeline—150 miles long—has been in operation in Mexico for over a year now. It has an initial capacity of transporting 500 tons/day which will be increased later to 1000 tons. The pipeline 14.8 cm. O.D. of carbon steel having a wall thickness of 0.219", which is increased to 0.25" in populated area, has an operating pressure of 1160 psig max. and 300 psig min. in the range 32 to 68°F. Ammonia is fed into the line through a pumping station having 6 pumps, 3 booster pumps each with a capacity of 157.5 gpm operating in parallel to feed the material and 3 horizontal centrifugal pumps which have similar capacity and despatch pressure of 960 psig. The line has one intermediate pumping station located in the midway provided with 3 horizontal centrifugal pumps in parallel. These pumps have a combined output of 4725 gpm at 747 psig. and are driven by diesel engines.

There is a similar pipeline connecting the ammonia plant at Carling in France and urea plant at Besch in W. Germany a distance of 52.4 km. The 4.5" O.D. ammonia pipeline has a wall thickness 0.141 to 0.156" into which liquid ammonia is fed through five centrifugal pumps in series which have a despatch pressure of about 53 atm. for a discharge rate of 560 tons/day. At Besch, the receiving end, the pressure is 23 atm. and no necessity has been found to provide any intermediate pumping station.

The Mid American Pipeline system has completed a major pipeline system, 850 miles in length, from Borger in Texas to Garner, Ogden and Sanborn in Iowa consisting of 6" and 8" of steel pipes having wall thickness 0.156" and average joint length of 60 feet. The initial capacity of transportation is 1300 tons/day of anhydrous ammonia which will be expanded to 3000-5000 tons/day with the installation of

additional booster stations. The operating pressure will be a maximum 1500 psig on the 6" portion and 1200 psig on the 8" portion of the line.

The steel used for the pipe contains a max. of 0.25 per cent carbon, 0.70-1.0 per cent manganese and 0.15 per cent copper. To hold copper within limits, the tube was normalized at 1600-1700°F.

Another long pipeline system about 2000 miles long under erection will connect major producing regions along Texas and Louisiana Gulf Coast to the Corn Belt. The maximum working pressures in the pipeline are 1407 psig for the 10" line, 1427 for the 8" and 1426 for the 6" line; the maximum operating pressure of 300 psig ensures that the ammonia remains in liquid state at the operating temperature of 35 to 75°F.

The development of anhydrous ammonia pipeline transportation system is tied to agricultural economics. The farmer has tried to improve his profit margin by increasing his yield through the use of anhydrous ammonia, which is convenient, economical and readily assimilated into the soil. The pipeline transportation system has the advantage of reaching ammonia to the consumer with the least amount of handling and transshipment.

[*Fertilizer News*, 14 (5) (1969), 25]

Dehumidified Building for Storage of Fertilizer

Three years' experience by TVA has been described regarding satisfactory bulk storage of hygroscopic fertilizers by providing proper protection against air of high humidity. Three systems that are used to protect fertilizers in large bulk storage buildings are as follows: (i) *Limited access of outside air*: For this bulk storage buildings should be built as airtight as possible. (ii) *Dehumidation of incoming air*: The entry of some air into a storage building can not be avoided. The problem can be avoided by feeding a small but steady stream of dehumidified air into the building which is accomplished by refrigeration to condense the moisture from the incoming air. (iii) *Heating of storage area*: A third method that is being used for humidity

control in bulk storage areas is the heating of incoming air without prior refrigeration. For example by maintaining temperature inside a storage building about 200°F above the outside temperature, the relative humidity of incoming air can be reduced from 100% to about 50%. Such practice however has not found wide use in this country probably because of high fuel requirements and the discomfort of such increased temperature in the summer.

Satisfactory Operation: TVA's dehumidified bulk-storage building was completed and placed in operation early in 1965. Operation since is reported to have been very satisfactory. This building is designed for storage of 20,000 tons of various granular fertilizers from TVA's granular combination fertilizer unit. Fertilizers stored include ammonium phosphate nitrates (30-10-0 and 25-25-0), ammonium nitrate sulphate (30-0-0-5S), nitric phosphates (20-20-0 and 26-13-0), and ammonium polyphosphate (15-61-0). Overall dimensions of the building are: length, 580 feet; width, 100 feet; vertical wall height, 48 feet; and peak height, 56½ feet. To a height of 20 feet, which is the intended level of filling, construction is of poured concrete with 9-inch wall thickness; the wall is strengthened by poured plasters every 20 feet. Above the 20-foot level, the framing is steel covered with protected, corrugated steel siding and roofing. This portion of the building is lined with 1½-inch thickness of glass fibre insulation with a vinyl vapour barrier toward the inside of the building. Purpose of the insulation is to conserve internal heat and to prevent moisture condensation on the walls during cold periods. Materials handling, both into and out of storage, is by means of an overhead travelling crane with a 187-cubic-foot (4½-ton) clamshell bucket. Movable partition walls 8 feet in height are provided across the width of the building; they can be placed with the crane at any desired location to provide separation between different products.

Control of Humidity: Humidity is controlled in the TVA building by pressurizing with dehumidified air. Ten points of air entry are provided around the periphery of the building, and each is equipped with a 5-ton refrigeration unit for dehumidification of the entering air. Maximum air flow through each unit is 2,000 cfm. This flow could be reduced to obtain a greater degree of dehumidification of the input air, but with the atmospheric conditions that prevail here this has

not been necessary. No air from within the building is recycled through the refrigeration machines; air discharge from the building is entirely by leakage through feed and discharge openings and a few other unavoidable plants. Recycling would result in dust fouling of the machines and increase the number required for pressurization of the building. The machines are of a standard, non-reheating type such as employed for commercial air-conditioning. Care was taken to select machines with aluminium-sheathed coils since nitric acid and ammonia fumes in the area would attack the usual copper coils. Reheating (location of condenser in outlet air stream), which would have involved purchase of nonstandard machines, was not considered necessary because calculations indicated that normal heat inputs to the building through product entry, lighting, crane operation, and solar radiation would be sufficient for reheating of the incoming air to temperatures at which its relative humidity would not exceed the critical relative humidities of the nitrates and other fertilizers planned for storage in the building. No heating system is provided in the building.

Experience has shown that because of the tightness of the building, it is never necessary to utilize more than five of the refrigeration machines. Thus, capacity of the installed system appears to be at least 100 per cent over actual requirements. During periods of low relative humidity, all machines frequently are turned off, and the building is operated without forced input of air. Temperature inside the building does not vary significantly with the diurnal cycle and usually remains 5° to 10°F above average outside temperature. Relative humidity has been in the range of 40 to 50 per cent which is well below the critical humidities of the fertilizers. Moisture analyses of nitrate fertilizers into and out of the building have indicated that some drying occurs during prolonged storage.

Installed cost for the refrigeration units and ducts was \$30,000, which amounts to \$1.50 per ton of fertilizer storage capacity. Experience now indicates that about one-half of this capacity would be sufficient under present conditions of operation.

[*The World of NPKS*, No. 30 (1968), 17]

Losses of Nitrogen by Volatilization

Gains in the total nitrogen content in the soil may occur by fertilizers addition and by various fixation processes. Again

nitrogen may be lost from the soil in different ways, viz. by volatilization, leaching, erosion, burning and crop removal. In particular, fertilizer nitrogen is susceptible to losses; in agricultural practice its recovery by the crop generally does not exceed 50 per cent. In the study of volatilization various techniques have been used and the lysimetre technique could be applied to detect volatilization.

By analyzing a large number of lysimeter experiments some general rules could be detected. Under controlled conditions of laboratory the technique of volatilization could be applied for reliable result. In volatilization three mechanisms are operative, viz. the direct volatilization of ammonia, the chemical decomposition of oxides of nitrogen and the enzymatic reduction of such compounds (denitrification). Volatilization may often be the result of an interaction of three mechanisms.

From investigation it appeared that loss of nitrogen is a chemical nature and both mineralized and fertilizer ammonia were susceptible to volatilization. Alkaline soil conditions were generally considered to be necessary for the occurred process. However recently volatilization of ammonia was also claimed to occur in acid soils. Volatilization was found to be stimulated by the presence of CaCO_3 . The heaviest losses due to ammonia volatilization are found in rather dry, light, sandy soils. Losses of added fertilizer ammonium can be reduced or entirely prevented if this ammonia is well mixed with soil. Volatilization of ammonia depends on associated anion. More ammonia is lost from ammonium sulphate than from ammonium nitrate. With ammonium phosphate only limited amounts were found to volatilize. Urea which is not itself volatile is very rapidly decomposed to ammonia in the soil by a number of microorganisms with increase activity like *Bacillus pasturii*.

During the nitrification process in the soil part of the nitrogen is lost. It is generally assumed that nitrogen losses during the nitrification process are the consequence of chemical decomposition of nitrite under more or less acid soil conditions. There are other explanations also. Our insight into the mechanisms involved is incomplete. Our knowledge of the intermediates formed in the nitrification process is still fragmentary. Reclaims that nitrite plays the predominant role in chemical decomposition reactions may come to be substantiated, but it remains

ture that the mechanisms of such decompositions are still only partly known. Particularly, the part played by soil organic matter and metallic ions in the decomposition is in need of clarification. Possibly more information can be obtained by the use of labelled nitrogen. In this way a differentiation can be made in the evolved gases between fertilizer nitrogen and soil nitrogen originating from such compounds as amino acids and amino sugars.

Losses by Denitrification: In denitrification, nitrate is used by micro-organisms as the terminal hydrogen acceptor in the dissimilation of organic compounds or in the oxidation of inorganic compounds such as H_2S and H_2 . Most investigations dealing with denitrification in soil concentrate on the microbial conversion of nitrate to the volatile reduction products i.e. N_2 , N_2O and NO . Denitrification may cause serious losses of nitrogen. The denitrification process in soil is principally continued to conditions of limited oxygen access. In addition to oxygen deficiency, the presence of sufficient hydrogen donor is required for the occurrence of denitrification in soil. From many results obtained in the laboratory it may be concluded that under the soil conditions it has been found that a higher denitrification rate occurred with amino acids than with carbohydrates. The favourable effect of amino acids on the denitrification rate was caused by a rapid hydrogen transfer to nitrate during deamination of amino acids.

In addition to creating anaerobic conditions in the rhizosphere plants were found to promote denitrification also by the excretion of hydrogen donors. pH of the soil influences the denitrification rate and the relative proportions of N_2 , N_2O and NO formed. Below pH 6 denitrification was markedly retarded N_2O being the main product. Above pH 10 and below 4.5 the process was found to be completely suppressed, while pH values of 7.0-7.5 were recorded as optimal. Temperature has also influence on denitrification rate. In the temperate humid regions the temperatures during the winter season are apparently too low for extensive denitrification, nitrate is much more susceptible to leaching during that period. In these regions the conditions for denitrification are much more favourable during varying periods in the summer. High denitrification losses can also be expected during rainy season in the tropical regions.

[J.W. Wolderdorp, *Losses of Nitro, stiktop*, (12), (1968) 32]

New Trends in the Technique of Nitric Acid Production

The demand for the production of nitric acid of 60-70 per cent concentration is increasing for the production of complex fertilizers. The new features designed by Johnson Construction Co, AB Stockholm give savings in operation costs without increased investment and high concentration nitric acid. Two features new to nitric acid technology incorporated are: (a) reduction in tower size using a new design of condenser and (b) production of 65 per cent HNO_3 concentration at 4 atm. pressure.

The nitric acid process can be divided into three stages: (a) combustion of ammonia (b) condensation of water formed (c) absorption of the nitrous gases in water. Johnson Construction Co.'s new design of the condenser has made it possible to reduce the size of the tower, the design makes it possible to produce nitric acid of 65 per cent concentration at 4 atm. pressure.

The unique feature of the plant as designed by the Johnson Construction Co. is a condenser of the lamella type. The heat exchanger permits an increase of the gas velocity and of the water vapour condensation rate. The water is furthermore separated in several steps as it is formed and this reduces the contact time between water and gas. The results obtained in a pilot plant have shown that it is possible to lower the concentration of " HNO_3 " ($HNO_3 + NO$ -gases calculated as HNO_3) to less than 9 per cent of the condensate. In this case the gas is cooled to about $24^\circ C$ at about 4 atm. Due to this improvement it is possible to reach a nitric acid concentration of 65 per cent instead of 55 per cent from the tower without increasing the tower height and the content of nitrous gases from the top of the tower. Despite the high velocity of the gas, the pressure drop is low due to the straight through flow.

The condenser is normally divided into three stages; the first two are cooled in counter current to the gas, by readily available cooling water at about $25^\circ C$, and the third stage by water at about $13^\circ C$ from the ammonia evaporator. The nitric acid formed is blue in the first stage, blue-green in the second stage and brown in the third stage, indicating that a considerable amount of NO is dissolved in the acid. The gas may be desorbed from the acid and returned to the bottom of the absorption tower by an additional process. In this way the nitric acid concentration in the condensate can be decreased even further. At a combustion pressure of 4 atm, the

concentration can be decreased to about 6 per cent in the condensate from stage I to III.

When designing the condenser, special attention was given to the pressure drop on the gas side, since this affects the operating costs. The total pressure drop in the condenser at 4 atm will be less than 500 mm. w.g. and by virtue of its design, it is possible to obtain very good heat transfer values, which is important, economically and functionally, in the design of a fast-cooling condenser. The first stage is physically divided into two parts. Up to the dew point of about $90^\circ C$ at 4 atm it is gas-water heat exchanger and from that point a condensing gas-water heat exchanger. As the dew point will rise with the pressure the gas-water heat exchange of stage I will decrease. For this reason the heat transfer coefficient of stage I will increase faster with pressure than that of stage II and III. The low values for stage III are due to the low partial pressure of the water vapour when the gas has left stage II.

The condenser has been designed as a lamella heat exchanger without any gaskets. Because of this type of design, it is possible to enlarge the exchanger uniformly, which means that a condenser for 200 t.p.d. HNO_3 will have the same hydraulic properties, heat transfer coefficient and pressure drops as a condenser for 10 t. p.d. HNO_3 . The guarantees which will be given for the heat exchanger are very reliable.

Johnson Construction Co. has designed a type of lamella coils with larger cooling surfaces to eliminate having a higher liquid level than is necessary in cases of, for instance, high cooling water temperature, or when producing 65 per cent nitric acid. The tube coils need much more space than the lamella coils with the same heating surfaces. The tube coils therefore must be placed in several layers under these conditions and because of this the liquid level height must be increased. The advantage with lamella coils is further accentuated when producing 70 per cent nitric acid at 7 atm pressure.

In a tower a diameter of about 4 m the depth of liquid on each sieve tray will be 60 mm for about $35 m^2$ cooling surface of the tube coils. For the same tower diameter and 55 mm level height this design allows a cooling surface of about $55 m^2$. Tube coils with the same cooling surface would require a level height of about 90 mm. The saving in static pressure achieved in this way represents about 30 per cent of the total pressure drop in the tower.

The pressure drop in the tower is a large part of the total pressure drop in the plant. The saving here in pressure drop, therefore, is of great importance in decreasing the operational costs. As the investment cost for the lamella-type exchanger is approximately the same as for tube coils with an equivalent heaving surface, a saving in operation costs is obtained without an increase in the capital cost.

The lamella design of both condenser and cooling coils requires attention to the mechanical construction of the equipment. Both the condenser and the lamella coils in the tower have, however, been designed for TIC-welding, and the thickness of the plate has been calculated to compensate for possible porosities in the welds through which leakage can occur.

Thus the heating surface of the condenser has been made 2.5-3 mm plate, which is almost double the normal tube wall thickness in tube heat-exchangers for this purpose. The heating surface itself is so designed that it is possible to make all the internal welds as TIC-welds on parallel combined plates. Such a weld is for this purpose superior to any other as it gives a thickness of the weld deposit that is heavier than or equal to the plate thickness. As the gas pressure in the equipment is always higher than the cooling liquid pressure, the root of the weld in this case will only be subject to pressure tension. It may be said that in a nitric acid plant, where corrosion and erosion factors are not critical, this condenser design has advantages over other types in that it is more efficient and offers greater reliability in service operation.

The above comments about the condenser also apply to the cooling coils in the tower, with the difference that these internal welds are of several types, i.e. the above mentioned TIC-welds together with hand-made metallic-arc joints of several types. There is, of course, the risk of slag inclusion in the latter type of welds for both tube and lamella coils, which under erosive action, can result in leakages. The effect of this possible defect has been limited in the lamella design, however, by dividing the cooling area of each sieve tray into six narrow units resembling foot-scrapers, each of which may be shut off from outside to be required at a suitable time.

By virtue of the above-mentioned process design improvements, the Johnson Construction Co. has developed a nitric acid process which should be of great interest to manufacturers of fertilizers and complex fertilizers, in particular. A further applica-

tion, of course, is the production of high concentration nitric acid by distillation of the 70 per cent acid. Thus, this process should enable more economic production of a wider range of acid concentrations than possible before.

On the plant side, the condenser, designed specifically for this application, may also find a useful place in the conventional autoclave (HK) method of high-strength nitric acid manufacture.

[*Nitrogen*, No. 57, January/February, (1969), 38 & 46]

Production of Sulphur from Calcium Sulphate

Sulphur can be produced as a saleable product from gypsum by reduction process together with co-produced carbonate or, by incorporating an ion-exchange operation using sodium chloride, sodium carbonate and calcium chloride can be obtained. Some recent investigations have been carried out by U.S. Bureau of Mines. Theoretical yields for the process are 0.186 s. ton sulphur, 0.615 s. ton sodium carbonate and 0.645 s. ton calcium chloride per s. ton of gypsum.

Gypsum is readily reduced to calcium sulphide by roasting with coal, natural gas, carbon monoxide or hydrogen at 900 to 950°C. At the present time work has been completed on reactions in a rotary kiln and, using bituminous coal, 94 to 98 per cent conversions have been achieved by this method. Formation of H_2S from the calcium sulphide is achieved by carbonating a 20 to 40 per cent waterslurry of the sulphide with carbon dioxide-bearing gases; these latter may be furnished by the flue gases from the reduction roaster. Hydrogen sulphide is evolved with the precipitation of calcium carbonate. In small counter-current combination tests which have been performed using a 50 per cent excess of carbon dioxide, 86 per cent conversion of CaS has been reported and the conversion could be increased to 95 per cent with almost stoichiometric use of carbon dioxide, if the equipment and operation techniques are sufficiently modified. The hydrogen sulphide produced by this method may be processed to elemented sulphur by the conventional Claus method. By incorporating an ion-exchange step into the process, calcium chloride and sodium carbonate can be produced as co-products instead of calcium carbonate by using sodium chloride.

In this modification, calcium sulphide is dissolved in water in the presence of recycled hydrogen sulphide to form cal-

cium bisulphide and this is then contacted counter-currently with an acid cation exchange resin to give sodium bisulphide in solution by ion-exchange. The resulting solution of essentially calcium free sodium bisulphide is then treated with the carbon dioxide-rich flue gases from the reduction kiln to give the hydrogen sulphide product together with precipitated sodium carbonate which is subsequently calcined to produce sodium carbonate. Finally, the resin, in the calcium form, is regenerated to the original sodium form by reaction with sodium chloride solution.

The calcium chloride solution thus produced can be evaporated to obtain the dried products in which case in addition to sulphur, sodium carbonate and calcium chloride are recovered as process products. As an alternative this calcium chloride may be used to form calcium sulphate from other sulphates which may be locally available.

The Bureau of Mines has estimated that, using coal at \$ 6 per short ton, the fuel cost per ton of recovered sulphur would be \$ 11, and that sulphur production costs would be about \$ 35 per short ton for a plant producing 330 s.t.p.d. Costs of \$ 30 and \$ 27 per s. ton sulphur are believed possible for production plants with rated capacities of 660 and 1,000 s.t.p.d. respectively.

By incorporating the ion-exchange step into the basic process and assuming a 90 per cent efficiency, the plant investment cost has been estimated at between \$ 20 and \$ 25 million, and operating costs at \$ 11 per short ton of gypsum (i.e. \$ 3.7 per ton of sulphur without credit for by-products). This takes into account requirements of 0.275 s. ton coal at \$ 6 per short ton and 0.7 to 1.0 short tons of salt ($NaCl$) at \$ 3 per short ton. In addition, for each short ton sulphur, 3.7 short tons of sodium carbonate are produced and, at \$ 20 per short ton, this provides a credit of \$ 74 per short ton sulphur (i.e. a zero sulphur cost).

In these estimates no credit value has been given to the calcium chloride which is produced at the rate of 3.9 short tons per short ton of sulphur and the cost of gypsum is assumed to be zero. The Bureau of Mines considers that gypsum could be mined and delivered to a sulphur recovery plant from an adjacent open pit mine for \$ 0.2 to \$ 0.4 per short ton.

[*Sulphur*, No. 80, Jan/Feb., (1969), 39]

Agro-Industrial Complex in India

In the first Lal Bahadur Sastri Memorial Lecture delivered at Indian Agricultural

Research Institute, New Delhi on April 7 1969, Dr. Vikram Sarabhai, Director, Indian Atomic Energy Commission, drew on the studies related to the implications of an agro-industrial complex based on low cost energy centres. Recent studies have indicated that new varieties of seeds yielded more crops only with substantial complementary inputs of chemical fertilizers and other plant nutrients, and they in turn required assured supplies of water at specified intervals without which the complementary inputs becoming infructuous. The Indian AEC has studied the implication of abundant low cost power to agriculture keeping in view a number of major electricity-consuming outlets, such as electro-chemical and electro-thermic processes and pumping of underground water through tube wells in addition to desalination of water.

In areas where underground water is available in plenty, like in the western U.P., the use of low cost electrical energy for lifting water along with modern agricultural

methods can make a crucial difference to the profitability of farming. This area covers a population of 23.6 millions and the soil is mostly alluvial. A suggested installation involves a power station with 2 nuclear reactors each of 600 MWe capacity, a fertilizer plant of total capacity of 4,500 tonnes/day and an aluminium plant of 150 tonnes/day with approximately 200 MWe used for lift irrigation through 36,000 tube wells. The total investment of the project is about Rs. 429 crores, the return on which is expected to be about 14 per cent. In arriving at this evaluation, differential tariff rates of 2 p/kWh for fertilizers, 2.6 p/kWh for aluminium and 10 p/kWh for tube wells have been assumed.

At this power cost for fertilizers, the project is comparable to a similar one based on coal even at a pit-head coal price of Rs. 35-40 ton. Though the power cost for the tube wells has been taken high, still the agricultural project gives sufficiently high returns. About 720,000 hectares are proposed to be irrigated under this project. The

total incremental cereal production would be 4.5 million tonnes and in addition 700,000 tonnes of pulses would also be produced. The implementation of the project would result in an increase in the per capita income in the area to the extent of Rs. 150/yr. The project by itself would contribute Rs. 486 crores to the GNP.

Since only about 50 per cent of the fertilizer production is utilized within the complex, the balance would be available for use outside. The benefits derived from this by way of increased food production, increased GNP, increased per capita income, etc. though high, are not included in the above figures. A plan of this type can be implemented in phases. While the nuclear power plant of a large capacity may take 5 to 6 years to complete, the pumping set could be energised much earlier through the installation of temporarily smaller conventional power units from district centres.

[*Nuclear India*, 7 (8) (1969), 3]

News in Brief

Production and Use of Fluid Fertilizers Made With Wet Process Superphosphoric Acid

Wet process superphosphoric acid containing 70% or more P_2O_5 , with about half the P_2O_5 present as polyphosphate, is being used for the production of fluid fertilizers with important advantages. The important advantages are higher concentration and product clarity because of the polyphosphate content. The acid can be used to produce liquid fertilizers of the following grades: 10-34-0, 8-8-8, 8-16-8 and 7-21-7. These liquids can be handled, stored and applied with typical commercial equipment. The acid can also be used to produce satisfactory suspensions such as 12-40-0, 15-15-15, 12-24-12, 10-30-10 and 3-10-30.

[Fert. Solns, 1968, 12 (4) July/Aug. 6-8, 10, 12, 14, *The World of NPKS*, No. 30, (1968), 27]

Conversion of Low Grade Phosphate Rock into Fertilizer by Bacteria Attack

Bacteria are being used in a new process for converting low-grade phosphate rock into useful fertilizer developed by the Commonwealth Scientific and Industrial Research Association of Australia. The product has been given the name of Biosuper and is proposed as a suitable alternative to superphosphate in Northern Australia, where there are deposits of low-grade phosphate rock and where there are also problems regarding high transport charges for imported superphosphates. The Biosuper is being produced by pelleting rock phosphate treated with sulphur and thiobacilli.

[*ibid*]

Patents*

Solution for Stabilizing Ammonium Nitrate: Marion L. Brown, A. W. Green,

*These patents have been reproduced from *Fertilizer Abstracts* published by the National Fertilizer Development Centre, Tennessee Valley Authority, Muscle Shoals, Alabama (USA) with kind permission of the Editor of FA. —Editor.

and E. L. Blanton (to Mississippi Chemical Corp.) U.S. 3,418,255, Dec. 24, 1968; 3 pp. Continuation of U.S. 3, 317, 276.

The earlier patent describes the manufacture of NH_4NO_3 prills stabilized against crumbling or caking due to crystal transitions. Stability is obtained by mixing small amounts of H_3BO_3 , $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$ with the melt of NH_4NO_3 before prilling. The present patent describes the preparation of a concentrated solution of the additives in a form that is easy to pump and mix with the melt and that will not clog the prilling orifices. In an example, an acid solution was prepared by mixing 2230 lb of 75% H_3PO_4 , 106 lb of 98% H_2SO_4 , and 3400 lb of water. This solution was ammoniated by introducing 414 lb of gaseous NH_3 . Then 2000 lb of powdered H_3BO_3 was mixed with the solution, followed by sufficient additional NH_3 to bring the molar ratio $NH_3:H_3PO_4$ to 1.8-2.0:1. The resulting solution had a pH of about 8 and contained 35-40% H_2O ; it remained quite fluid at temperatures as low as 70°F. Mixing of 10 lb of this solution/ton of NH_4NO_3 gave a suitable dosage of stabilizing additives in the prills, namely 0.2% $(NH_4)_2HPO_4$, 0.01% $(NH_4)_2SO_4$, and 0.18% H_3BO_3 . These additives also stabilize mixed fertilizers containing NH_4NO_3 .

[*Fertilizer Abstracts*, 2 (2) (1969) 22]

Ammonia Synthesis: A. M. Fayon and J. B. Goldstein (to American Cyanamid Co.) U. S. 3, 409, 397, Nov. 5, 1968; 3pp.

NH_3 is produced by reacting H and N in the presence of $LiNH_2$ at pressures of at least 2400/psig and temperatures of 350-500°. Under these conditions, Li_2NH produced by the NH_3 forming reaction, is converted to $LiNH_2$ by reaction with additional H and N. The principal reactions are: $4LiNH_2 + 3H_2 + N_2 \rightarrow 2Li_2NH + 4NH_3$ and $2Li_2NH + 3H_2 + N_2 \rightarrow 4LiNH_2$. In order to achieve continuous production of NH_3 the reaction is maintained at or above a critical operating pressure for regeneration of the $LiNH_2$. This critical pressure has been found to be at least 2400

psig. Generally, the higher the pressure above 2400 psig the greater the yield of NH_3 at a given temperature. Because of equipment limitations the preferred operating pressure is from about 2500-3500 psig. The preferable temperature is 400-450°, and the H is present in 5-25% of a mole excess. The space velocity of the reaction mixture gas is between 20,000 and 40,000 reciprocal hours. Operating data are tabulated.

[*ibid.*, 23]

Recovering Fluorides from Vapours: William E. Rushton and George Kleinman (to Whiting Corp.) U.S. 3,415,039, Dec. 10, 1968; 7 pp.

Fluoride-containing vapors from the evaporation-concentration of dilute wet-process H_3PO_4 are scrubbed with an aqueous solution of H_2SiF_6 at a pressure lower than that in the evaporation chamber whereby larger amounts of the gaseous fluorides are absorbed than by usual methods. Thus, in a 3-stage evaporator system for producing H_3PO_4 containing 54% P_2O_5 the first stage was operated at 155°F. and 8.56 in. Hg absolute. The vapors were scrubbed at a pressure of 2.0 in. Hg absolute to produce 25% H_2SiF_6 . The loss of F in the scrubbed vapors was 0.004 lb F/lb H_2O vapor, compared with 0.025 lb F/lb H_2O vapor by usual method. Similarly, a loss of 0.0085 lb F/lb H_2O vapor was obtained when producing 30% H_2SiF_6 compared with a loss of 0.06 lb F/lb H_2O vapor by usual methods. Apparatus is described.

[*ibid.*, 25]

Purification of Phosphoric Acid: D. S. Bunin, F. J. Kelso, and R. A. Olson (to FMC Corp.) U.S. 3,410, 656, Nov. 12, 1968; 4 pp.

Impure wet-process H_3PO_4 is extracted with a solution of tri-in-butylphosphate in kerosene or N-hexane. The resulting organic solution containing 50-85% of the P_2O_5 originally present in the wet-process acid is then contacted with relatively pure aqueous H_3PO_4 whereby metal impurities are selectively removed from the organic

solution of H_3PO_4 . The purified organic solution of H_3PO_4 is then stripped with water whereby pure aqueous H_3PO_4 is obtained as product. The impure wet-process acid used as feed to the process is preferably pretreated to remove residual sulfate and fluosilicate impurities by usual methods. In an example, impure acid containing 43.63 P_2O_5 , 0.33 CaO , 1.4 SO_4 , 0.7 F, 1.41 Fe_2O_3 , 3.1 R_2O_3 , and 0.4% SiO_2 was purified to give a product acid containing 33.57 P_2O_5 , 0.04 SO_4 , 0.0098 Fe_2O_3 , 0.0114% R_2O_3 , a trace of F, and no SiO_2 .

[*ibid.*, 26]

Wet-Process Phosphoric Acid: Harold B. Caldwell (to Whiting Corp.) U.S. 3, 416, 889, Dec. 17, 1968; 19 pp.

A reactor vessel is described for acidulating phosphate rock with H_2SO_4 to prepare H_3PO_4 . The reactor is comprised of a vertical cylindrical shell, a central forced-circulation draft tube of large diameter, and a vapor space at the top connected with a barometric condenser. The phosphate rock, preferably premixed with dilute recycled H_3PO_4 , is fed continuously into a side of the vessel. The mixture flows upwardly to the vapor space between the wall of the vessel and the draft tube. Feed H_2SO_4 is sprayed onto the surface of the liquid in the vapor space and the mixture flows downwardly through the draft tube. Reaction slurry is continuously pumped to a filter feed tank; gypsum filtration is conventional. Maintenance of a large body of rapidly circulating slurry in the reaction vessel and the evaporative cooling that occurs below atmospheric pressure in the vapor space cause uniform removal of reaction heat, resulting in better filterability of the slurry. Apparatus is described.

[*ibid.*]

Ammonium Phosphate: David M. Young (to Dow Chemical Co.) U.S. 3, 415, 619, Dec. 10, 1968; 3 pp.

A solution of H_3PO_4 in a H_2O -immiscible organic solvent, prepared by liquid-liquid extraction of an HCl , HNO_3 , or H_2SO_4 acidulate of phosphate rock, is ammoniated whereby ammonium phosphate crystals are formed in the organic solution. Thus, phosphate rock was treated with aqueous HCl and the solution was filtered. The filtrate, containing phosphate 16.8, chloride 24.7, Ca 12.6, and Fe 1% wt was treated with gaseous Cl to oxidize the Fe. The solution was then treated to remove Fe by liquid-liquid extraction with a 0.1M solu-

tion of tricaprylyl amine in a petroleum fraction. The aqueous phase containing (5 ppm Fe was separated and treated to dissolve the H_3PO_4 by liquid-liquid extraction with a 50 volume % solution of tri-n-butyl phosphate in a petroleum fraction. The organic phase containing 4% H_3PO_4 was then treated to remove Ca by liquid-liquid extraction with H_2O . The resulting organic phase containing (40 ppm Ca was ammoniated by bubbling an excess of gaseous NH_3 through the solution at 26-36°, precipitating crystalline $(\text{NH}_4)_2\text{HPO}_4$. The crystals were filtered from the organic extractant, washed with N-pentane, and dried to produce a completely H_2O -soluble product containing 2.8% chloride. A substantially chloride-free product was obtained by washing with liquid anhydrous NH_3 .

[*ibid.*, 27]

Purification of Hydrogen: Kwo T. Lee (to Chemical Construction Corp.) U.S. 3, 420, 633; Jan. 7, 1969; 5 pp.

An improved method is described for regenerating aqueous triethanolamine solution used to scrub H_2S and CO_2 contaminants from H produced by steam reforming of hydrocarbons. The spent solution from a pressure scrubber is sent through power-producing turbine which discharges the solution at 35-60 Kg/sq. cm. The discharged liquor is passed through a gas-liquid separator where a gas rich in H is separated. This gas is recompressed and recycled to the scrubber. The liquor from the separator is sent through a second turbine which discharges the liquor at 5-20 kg/sq. cm. Passage through a second gas-liquid separator yields substantially pure CO_2 directly usable for urea synthesis. The liquor is then passed through a third turbine where the pressure is reduced to less than 5 kg/sq. cm and a gas phase rich in H_2S is separated. The liquor is then sent to a steam-heated stripping tower to complete the regeneration.

[*Fertilizer Abstracts*, 2 (3) (1969), 47]

Ammonium Humate Fertilizer: Albert M. Cooley. U.S. 3,418,100, Dec. 24, 1968; 3 pp.

Leonardite ore containing metal humates is converted to ammonium humate fertilizer by (1) treatment with H_3PO_4 in an amount sufficient to release humic acid from the metal humates but not so much as to convert the mixture to a slurry; (2) reaction with NH_3 , preferably in a rotary drum

granulator, and (3) drying the granules. Other fertilizer materials may be added to increase the plant nutrient content of the mixture. In an example, leonardite ore 1453, 75% H_3PO_4 450, NH_4NO_3 300, and KCl 150 lb were tumbled in a rotary drum to give damp granules; 84 lb NH_3 was then introduced, after which the ammoniated granules were dried in a rotary drum granulator to a H_2O content of 16%.

[*ibid.*]

Phosphoric Acid: Klockner-Humboldt-Deutz A. G. (by Wilhelm Reulecke, Toni Litzenburger, and Otto Winter.) *S. Afr.* 68/0811, July 2, 1968; 5 pp.

Apatite is digested with H_3PO_4 and the resulting solution is treated to remove Ca $(\text{H}_2\text{PO}_4)_2$ by crystallization. The mother liquor is then ammoniated to pH 3.8-4.0 whereby Fe and Al impurities are precipitated. The solution is filtered, and the filtrate is contacted with a cation exchange resin in the H form whereby H_3PO_4 in high purity is obtained. Thus, 1.22 kg of mother liquor containing 61.3 H_3PO_4 , 5.65 FePO_4 , and 13.45% AlPO_4 was treated with 0.13 kg gaseous NH_3 with addition of 0.8 kg H_2O to prevent crystallization of the resulting $\text{NH}_4\text{H}_2\text{PO}_4$. The solution (pH 3.8-4.0) was filtered and the filter cake was washed with 1.25 kg H_2O . The combined filtrate and washings weighed 3.15 kg and contained 0.88 kg $\text{NH}_4\text{H}_2\text{PO}_4$. It was passed through a strongly acid cation exchange resin in the H form. Product solution comprised of 0.79 kg H_3PO_4 in 2.22 Kg H_2O can be made in this way. The process can be used to prevent buildup of impurities in the recirculating mother liquor used in the manufacture of $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

[*ibid.*, 49]

Corrosion Inhibitor for Phosphoric Acid: W.P. Banks (to Continental Oil Co.) U.S. 3,414,376, Dec. 3, 1968 4 pp.

Corrosion of mild steel by merchant grade wet-process H_3PO_4 is inhibited by the addition of at least 50 ppm of iodide ion and about 2-35 wt % H_2SO_4 . For example, the corrosion rate of 1020 mild steel in 76% wet-process H_3PO_4 at 120°F. was 1918 mpy. Addition of 200 ppm of KI, NaI, NH_4I , or HI reduced the corrosion rate to 153 mpy. Other corrosion data are given, including two graphs.

[*ibid.*, 50]

Ammonium Phosphates: James E. Barker (To Tennessee Corp.) U.S. 3,420, 623, Jan. 7, 1969; 6 pp.

High-purity $\text{NH}_4\text{H}_2\text{PO}_4$ or $(\text{NH}_4)_2\text{HPO}_4$ are prepared from impure wet-process H_3PO_4 by a process comprised of stepwise precipitation and removal of impurities, ammoniation under pressure to precipitate $(\text{NH}_4)_7\text{H}_2(\text{PO}_4)_3$, and heating of the $(\text{NH}_4)_7\text{H}_2(\text{PO}_4)_3$ to prepare $\text{NH}_4\text{H}_2\text{PO}_4$ or $(\text{NH}_4)_2\text{HPO}_4$. Thus, 4220 lb wet-process acid containing 40% H_3PO_4 , 2.6% F, and traces of other impurities was mixed with 103 lb NaCl and the temperature was held at 140°F. The resulting Na_2SiF_6 precipitate was removed and the clarified acid containing 38% H_3PO_4 was continuously ammoniated to pH 5.5 while maintaining the temperature at 217°F. The resulting precipitate was filtered off, washed, and dried, yielding a by-product containing 46.3% P_2O_5 and 7.4% N suitable for use as fertilizer. The filtrate was further ammoniated to pH 9 with NH_4OH and centrifuged to remove precipitated impurities. The solution was then further ammoniated at 45 psig and 140°F. with gaseous NH_3 , the resulting precipitated $(\text{NH}_4)_7\text{H}_2(\text{PO}_4)_3$ was filtered off. Drying at 180°F. in an NH_3 atmosphere at a pressure of 33 mm. Hg gave a product containing 99.1% $(\text{NH}_4)_2\text{HPO}_4$.

[*ibid.*, 50]

Ammonium Polyphosphate: Elliot B. Fitch (to Dorr-Oliver Co.) U.S. 3,420, 624, Jan. 7, 1969, 3 pp.

A process for the manufacture of ammonium polyphosphate consists of mixing commercial H_3PO_4 (50-58% P_2O_5) with gaseous NH_3 and recycled preheated (300-325°F.) reaction product in a pipe reactor. The reaction product is discharged at about 325°F. and a pH of about 1.5 and enters a receiver where steam is vented. The liquid is pumped from the receiver, about 2% is split from the stream, heated to about 325°F. in a heat exchanger, and recycled to the pipe reactor. The remainder is fed, with additional NH_3 vapor in excess, to a second pipe reactor. The reaction product is discharged from the second reactor at 450-500°F. and enters a second receiver where steam and unreacted NH_3 are separated, leaving a melt that solidifies on cooling. The product contains 11-12% N and 58-60% P_2O_5 . About 50% of the P_2O_5 is in non-orthophosphate form.

[*ibid.*]

Ammonium Phosphate Fertilizers: J. D. Crowther and S. M. Janikowski (to Fisons Fertilizers Ltd.) U.S. 3, 415, 638, Dec. 10, 1968, Brit. Appl. Mar. 26, 1964; 3 pp.

Phosphoric acid (40-52% P_2O_5) is reacted with gaseous NH_3 under a pressure of 20-35 psig to give a fluid solution that, on releasing the pressure, loses sufficient H_2O to give a solid product. The mole ratio $\text{NH}_3:\text{H}_3\text{PO}_4$ is within the range 1:1-1.5:1. For example, a stirred tank ammoniator at 25 psig was charged with 50 lb/hour of H_3PO_4 (50% P_2O_5) and 6 lb/hour NH_3 . A solution was formed at its boiling point, 165°, containing 13% H_2O ; this level of H_2O was maintained by adding small amounts of H_2O . The solution was discharged through an expansion nozzle into a chamber at atmospheric pressure whereupon solid ammonium phosphate was obtained having a H_2O content of 8%. By discharging the solution from the pressure reactor onto a moving bed of other fertilizer materials, granular mixed fertilizers such as 22-11-11 are obtained.

[*ibid.*,]

Adding Micronutrients to Granular Fertilizers: Otis D. Philen, Julius Silverberg, and Melvin M. Norton (to Tennessee Valley Authority). U.S. 3,423,199, Jan. 21, 1969; 7 pp.

Granular micronutrient fertilizers are mixed with pulverized micronutrient compounds in the presence of a concentrated aqueous solution that interacts to bond the micronutrients firmly to the surface of the granules. The interaction may be chemical or physical or both. Thus, granular NH_3NO_3 was mixed with 10% ZnO and 2.5% kieselguhr in a rotary mixer for 1 minute while spraying with aqueous 70% NH_4NO_3 solution. The product was comprised of NH_4NO_3 coated with crystalline $\text{Zn}_5\text{NH}_4(\text{NO}_3)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ which held the unreacted portion of the ZnO in a tightly bonded coating. In another example, granular triple superphosphate and 13% of a mixture of powdered oxides of Zn, Mn, and Fe was sprayed in a rotary mixer with aqueous 2.8% NH_4 -polyphosphate solution. The product granules had a smooth adherent coating of the micronutrients.

[*ibid.*, 52]

Nangal Unit of F.C.I.

The Nangal fertilizer factory will be expanded using a new feedstock, viz. low sulphur heavy stock (LSHS), as the conventioned feedstock like petroleum and coal are not easily available in Punjab.

With oxygen available from the existing electrolysis plant, LSHS, which is available

in abundance, will be a good choice. It is a heavy fraction of crude and is left out after naphtha, gasoline and diesel oil have been taken out during the distillation of crude in the refinery. Nangal is expected to have a capacity of 152,000 tonnes of nitrogen a year, which will bring the total annual installed capacity to 232,000 tonnes of nitrogen.

This unit has broken all previous records by producing 14, 281 Kg. of heavy water against the installed capacity 14,100 Kg. The target of fertilizer production for the year has also been exceeded—CAN production has been 309,241 te (25% N) against the target of 308,000 te. It has also won the National Safety Award for the fourth year in succession.

[*Lokudyog*, 3 (2) (1969), 155]

Trombay Fertilizer Factory

For the first time Trombay unit of FCI Ltd. has recorded a profit of Rs. 53 lakhs in 1968-69 and sold ammonium bicarbonate and methanol in the overseas market. Orders of the value of Rs. 10 lakhs have been secured. The year 1968-69 marks the beginning of progressive improvement in production, sales and financial results for which credit must go to Trombay technologists who on the failure of the foreign contractors took upon themselves the task of remedying the deficiencies. A good part of the corrective action required on ammonia, urea, complex fertilizer and methanol plants has already been completed and as a result the ammonia and methanol plants are in a position to attain full capacity as soon as the supplementary facilities are completed. The complex fertilizer plant has been completely recast on a new process developed by FCI technologists and worked consistently above the rated capacity. The shortages of ammonia however restricted production.

The scheme for diversification into industrial chemicals initiated in 1966-67 had made considerable headway. In the first phase, specification products for industry for ammonia, nitric acid, sulphuric acid and technical grade urea and argon were produced and marketed.

1968-69 saw the production of two derivatives recovered from waste carbon dioxide viz. ammonium bicarbonate and liquid carbon dioxide for aerated water and beverage industry and for food, pharmaceutical and bakery industry. Two new plants, viz. a carbon black and concentrated nitric acid plants are under

construction and a contract for a methyamine plant has been finalized. All these 4 plants are being built almost entirely with indigenous resources. The know-how for ammonium bicarbonate and carbon black was developed by the Planning & Development Division of FCI. Ltd.

During 1968-69, two new complex fertilizers were introduced in the SUPHALA series i.e. a complete fertilizer 15-15-15 and

18-18-9 in addition to 20-20-0. These three contain three secondary nutrients, viz. sulphur, magnesium and calcium and can be used on all soils and crops.

For balancing the existing plants a phosphoric acid plant and a naphtha re-former furnace to supplement gas deficiencies in ammonia and methanol plants are being built, based largely on the know-how developed by FCI itself.

FCI Catalysts for Export

Planning & Development Division of the Fertilizer Corpn. of India Ltd., have recently secured and signed a contract with a European country for the export of a range of fertilizer catalysts, being manufactured in their plants at Sindri, in the face of competition from European manufacturers. The catalysts being exported are primary and secondary reformation catalysts, high and low temperature. CO-conversion catalysts and methanation catalyst.

YEARLY PRODUCTION SINCE COMMISSIONING OF THE PLANT, TONNE

Year	Ammonia	Urea	Complex Fertilizer in terms of 20-20-0	Methanol
1965-66*	12,274	8,064	11,184	Nil
1966-67	57,855	53,188	51,194	2,586**
1967-68	65,958	57,436	86,859	9,620
1968-69	77,820	68,520	110,000	17,380†

*Plants went in commercial production for 5 months only.

**Plants went in commercial production for 6 months only.

†Inclusive of 2,290 te of equivalent methanol as reformed gas supplied for making ammonia.

[Lokudyog, 3 (2) (1969), 153]

FCI Accord with a German Process

Fertilizer Corpn. of India Ltd., and Heinrich Koppers of Essen (W. Germany) have signed an agreement in New Delhi to use the well-known Kopper-Totzek gasification process for setting up coal-based fertilizer plants in India. The main advantage of this process is that low grade coal with an ash content as high as 50 per cent can be used for economic production of synthesis gas. The first use in India of this process will be at the proposed 900 tons/day coal-based ammonia plants already approved in principle by the Government.

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STATISTICS

TABLE 1—NAPHTHA AVAILABILITY POSITION IN INDIA BY 1974

(In Million Tonnes/yr.)

Area Refinery	Total	ABC AREA				KKO		Bombay & Goa		Cochin	Madras	Vizag	All India Excess Demand over Production	
		Sub-Total	AOC	Gauhati	Barauni	Haldia	Koyali	Sub- Total	BSR					ESSO
										CRL	MRL	Caltex		
A. Crude Throughput	26.800	8.500	0.500	1.100	3.400	3.500	4.250	6.450	3.750	2.700	3.500	2.850	1.250	
B. Production														
(i) A.T.F.	1.038	0.206	—	0.018	0.032	0.156	0.216	0.390	0.192	0.198	—	0.148	0.078	
(ii) Kerosene	3.710	0.895	0.090	0.112	0.317	0.376	0.854	0.739	0.487	0.252	0.805	0.295	0.122	
(iii) Motor Spirit	1.782	0.732	0.090	0.181	0.221	0.240	0.227	0.419	(N.A.)	(N.A.)	0.176	0.152	0.076	
(iv) Naphtha	2.529	0.661	—	—	0.339	0.322	0.530	0.562	(N.A.)	(N.A.)	0.349	0.333	0.094	
C. Demand														
(i) A.T.F.	1.038	0.194					0.394	0.390			0.010	0.048	0.002	NIL
(ii) Kerosene	4.387	1.130					1.063	1.044			0.448	0.366	0.336	(-) 0.677
(iii) Motor Spirit	1.782	0.732					0.227	0.419			0.176	0.152	0.076	NIL
D. Naphtha Available														
	2.529	0.661			0.339	0.322	0.530	0.562	(N.A.)		0.349	0.333	0.094	
(1) Petrochemicals														
Barauni-Aromatics	0.100	0.150			0.100									
Haldia-Methanol	0.050	0.050				0.050								
Kota-PVC	0.060						0.060							
Koyali-Aromatics	0.134						0.134							
Naphtha-Cracker	0.360						0.360							
Bombay-UCIL	0.130							0.130						
-do- NOCIL	0.300							0.300						
Trombay Methanol	0.040							0.040						
Calico-PVC	0.050							0.040						
Tuticorin PVC	0.020							0.050			0.020			
Total for Petrochemicals	1.244	0.150			0.100	0.050	0.554	0.520			0.020			
Naphtha available for fertilizers	1.285	0.511			0.239	0.272	(-)0.024	0.042			0.329	0.333	0.094	

N.B. ABC—Assam, Barauni and Calcutta; KKO—Kandla, Koyali and Okha.

[Planning Department, P & D Division, FCI Ltd., Sindri]
March '69

TABLE 2—NAPHTHA AVAILABILITY FOR FERTILIZER PLANTS

	Production Figures: Demand Figures :		Projections by 1974 Licensed Capacity for Fertilizers						
			(In Million Tonnes/yr.)						
	Nitrogen Capacity	Total	Assam/ Barauni	Haldia	Koyali	Bombay- Goa	Cochin	Madras	Vizag
<i>Naphtha available for fertilizers</i>		1.285	0.239	0.272	(—)0.024	0.042	0.329	0.333	0.094
<i>Demand for fertilizers</i>									
FCI—Gorakhpur	0.080		0.080						
FCI—Barauni	0.152		0.160						
ICI—Kanpur	0.200		0.200						
Birla—Mirzapur	0.160		0.160						
FCI—Sindri	0.020			0.020					
HSL—Rourkela	0.050			0.050					
FCI—Durgapur	0.152			0.160					
-do- —Haldia	0.152			0.160					
GSFC—Existing	0.120				0.040				
Expansion	0.120				0.120				
Kota—DCM	0.130				0.130				
FCI—Trombay (Existing)	0.090					0.090			
-do- -do-(Expansion)	0.253					0.264			
Zuari—Goa	0.160					0.160			
FACT—Alwaye	0.092						0.095		
FACT—Cochin	0.152						0.160		
Mangalore	0.152						0.160		
EID—Ennore	0.016							0.016	
Madras Fertilizers	0.190							0.249	
Coromandel (Existing)	0.080								0.080
-do- (Expansion)	0.152								0.160
Occidental	0.152								0.160
Total		2.874	0.600	0.390	0.290	0.514	0.415	0.265	0.400
Nett Deficit		1.589	0.361	0.118	0.314	0.472	0.086	(—)0.068	0.306

(Planning Department, P & D Division., FCI Ltd., Sindri)

TABLE 3.—INVESTMENT IN THE FERTILIZER INDUSTRY (ESTIMATE)

Investment-Year	Total Available Capacity at the End of the Period ('000 tonnes)		Public Sector	Private Sector	Total
	N	P ₂ O ₅	Rs. Crores		
a. Investment up to the end of March 1951	16.5	19.8	18	2	20
b. 1951-56	98.8	45.3	37	3	40
c. 1956-61	238.4	82.5	57	3	60
d. 1961-66	542.9	213.7	145	30	175
e. 1966-69	1024.0	421.0	100	150	250
			357	188	545
f. 1969-74	5150.0 (3730)	2330.0 (1735)	750	550	1300*
g. 1974-79	7750.0 (6635)	4200.0 (3310)	—	—	900

(Figures in brackets are consumption targets.)

*Out of Rs. 1,300 crores, Rs. 490 crores will be in foreign exchange.

[Kasturirangan, V. N., *Fertilizer Scene—IV Plan, Proc. No. 2, Fertilizer Inst., (Fert. Assn. of India, New Delhi), April 1969, 5]*

TABLE 4—TARGETS & ACHIEVEMENTS OF AGRICULTURAL DEVELOPMENT PROGRAMMES DURING 1966-71, 1966-67, 1967-68 & 1968-69

Programmes	Unit	1966-71	1966-67	1967-68		1968-69	
		Target	Target	Achievement	Target	Anticipated achievement	Target
Major and Medium Irrigation (Addl. area)	 Million hectares	3.6	1.4	1.4	1.4	1.4	1.5
Minor Irrigation (Additional area benefited)†	 "	6.9	1.5	1.4	1.6	1.4	1.4
Soil Conservation on Agricultural Lands (Addl. area benefited)	 "	8.1	0.47	0.14	0.24	0.15	0.17
Land Reclamation (Additional area)	 "	1.0	—	—	—	—	—
High Yielding Varieties of Imported Seeds of Foodgrains*							
(a) Paddy	 "	5.2	1.3	0.9	2.5		
(b) Wheat	 "	3.2	0.6	0.5	1.4		
(c) Hybrid Maize	 "	1.6	0.4	0.2	0.7	6.1	
(d) Hybrid Jowar	 "	1.6	0.4	0.2	1.0		3.0
(e) Hybrid Bajra	 "	1.6	0.1	0.1	0.5		
Total	 "	13.2	2.8	1.9	6.1	6.1	8.5
Multiple Cropping*	 "	12.1			3.0	2.9	6.1
Consumption of Chemical Fertilizers*							
(a) Nitrogenous (N)	 Lakh tonnes	24.0	10.0	7.4	13.5	10.4††	17.0
(b) Phosphatic (P ₂ O ₅)	 "	10.0	3.7	2.5	5.0	3.4	6.5
(c) Potassic (K ₂ O)	 "	7.0	2.0	1.1	3.0	1.7	4.5
Urban Compost*	 Million tonnes	5.6	4.2	3.7	4.1	3.9	4.6
Green Manuring	 "	12.9	10.6	8.1	9.8	8.8	10.3
Plant Protection (Gross area)	 "	85.0	25.5	24.3	51.0	36.4	54.6

†Includes new irrigation stabilisation of old irrigation area benefited by drainage, flood and sea water protection schemes etc.

*Level reached by the end of the period mentioned. ††Actual achievement.

[Indian Agriculture in Brief (Ministry of Food, Agric. CD & Coop., Govt. of India, Delhi), 1968, 174]

TABLE 5.—AVERAGE SIZE OF HOLDINGS

Country				Year	Hectares
Belgium	..	..	..	1951	6.6
Denmark	..	..	..	1959	15.8
Germany (Federal Republic)	..	..	..	1960	9.5
INDIA	..	..	..	1961-62	2.6
Japan	..	..	..	1960	1.2
New Zealand	..	..	..	1959-60	231.6
Norway	..	..	..	1959	17.5
Sweden	..	..	..	1961	14.6
U.K.	..	..	..	1960-61	40.6
U.S.A.	..	..	..	1959	122.5
Yugoslavia	..	..	..	1950	4.7

Note: Arrived at after dividing the area of Holdings by the total number of Agricultural Holdings.

Source: F.A.O. Year Book of Production.

[*Indian Agriculture in Brief* (Ministry of Food, Agric. CD & Coop. Govt. of India, New Delhi), 1968, 234]

TABLE 6—GROWTH OF THE INDIAN PETROLEUM INDUSTRY

Year				Imports, Rs. Crores			Exports, Rs. Crores
	Consumption, 1000 tonnes	Production of Crude Oil, 1000 tonnes	Refineries Crude Charged, 1000 tonnes	Crude	Products	Total	
1950	..	..	251	Nil	51.84	51.84	2.25
1955	..	..	3,335	24.31	60.53	84.84	3.55
1960	..	..	6,091	40.57	38.09	78.66	4.61
1961	..	..	6,440	39.31	44.23	83.54	3.76
1962	..	..	7,003	38.72	48.77	87.49	3.85
1963	..	..	8,138	41.78	54.81	96.59	5.50
1964	..	..	8,932	42.59	53.78	96.37	4.84
1965	..	..	9,754	40.38	44.73	85.11	3.92
1966	..	..	12,030	56.10	51.31	107.41	8.76
1967	..	..	14,430	79.59	39.67	119.26	14.22

[*Indian Petr. and Chemicals Statistics 1967* (Econ. & Stats. Divn. Ministry of Petroleum & Chemicals, New Delhi), 1969, ix]

TABLE 7.—CAPITAL EMPLOYED† IN THE INDIAN PETROLEUM
INDUSTRY AS ON 1.1.66

(Rs. Crores)

	Indian Capital			Foreign	Total
	Govt. capital	Other capital	Total		
1. Paid up Capital & reserves ..	197.71	2.70	200.41	140.83	341.24
2. Debentures ..	30.00	10.71	40.71	0.09	40.80
3. Total ..	227.71	13.41	241.12	140.92	382.04
4. Other Capital*	94.49	102.84	197.33	42.59	239.92
5. Grand Total	322.20	116.25	438.45	183.51	621.96

[Indian Petroleum & Chemicals Statistics
1967 (Econ. & Statistics Div., Ministry of
Petroleum & Chemicals, New Delhi), 1969, 35]

TABLE 8—COST COMPARISON OF SULPHURIC ACID PRODUCTION FROM PYRITES AND GYPSUM

Pyrite Based Sulphuric Acid Plant			Gypsum Based Sulphuric Acid Plant		
Direct operating costs:		\$/s. ton	Direct operating costs:		\$/s. ton
(1) Labour (operating), 32 men ..	0.63		(1) Labour (operating and maintenance), 24 men ..	0.47	
(2) Utilities			(2) Utilities		
Electrical power, 105 kWh/s. ton ..	1.05		Electrical power, 101 kWh/s. ton	1.01	
Boiler water, 400 gal/s. ton ..	0.08		Natural gas, 14.0 m.m. Btu/s. ton	5.60	
Cooling water, 3,080 gal/s. ton ..	0.15		Oxygen, 0.34 s. tons/s. ton ..	2.72	
Lime for pond ..	0.10		Boiler water, 600 gal/s. ton ..	0.15	
			Cooling water, 4,600 gal/s. ton ..	0.23	
(3) Maintenance labour & supplies			(3) Maintenance labour & supplies		
Acid plant, 4.5% annually ..	1.02/s. ton		Acid plant, 4.5% annually ..	1.24/s. ton	
Rest of plant, 3.0% annually ..	0.68/s. ton		Rest of plant, 2.0% annually ..	0.56/s. ton	
Total direct costs ..	3.71		Total direct costs ..	11.98	
Indirect costs, 16.6% annually of total investment ..	4.58		Indirect costs, 16.6% annually of total investment ..	5.70	
Direct & Indirect costs ..	8.29		Direct & indirect costs ..	17.68	
By-product steam (low pressure), 1,440 lb/s. ton acid ..	-0.72		By-product steam (low pressure), 2,000 lb/s. ton ..	-1.00	
Net conversion costs ..	7.57		Net conversion costs ..	16.68	
Raw material, 0.686 s. ton pyrite (50% S) per s. ton acid (95% recovery) ..	4.12		Raw material, Gypsum ..	0.00	
Total Costs ..	11.69		Total costs ..	16.68	

[Sulphur, No. 80, January/February, (1969), 22]

TABLE 9—LIST OF FERTILIZER PLANTS IN PRODUCTION, UNDER IMPLEMENTATION, LICENSED & PROPOSED

Sl. No.	Name of Factory	End Product	Annual capacity Tc/yr.	Nutrient/year, Tonnes	
				N	P ₂ O ₅
A. FACTORIES IN PRODUCTION					
(a) Public Sector					
1.	FCI, Sindri	.. Amm. Sulphate	3,55,000		
		Amm. Sulphate Nitrate	1,21,920	1,17,000	—
		Urea	24,000		
2.	FCI, Nangal	.. Cal. Amm. Nitrate (25% N)	3,20,000	80,000	—
3.	FCI, Trombay	.. Urea	99,000	90,000	45,000
		Nitro-phosphate	2,70,000		
4.	FCI, Gorakhpur	.. Urea	1,79,320	80,000	—
5.	FCI, Namrup	.. Urea	55,000		
		Amm. Sulphate	1,00,000	45,000	—
6.	FACT, Alwaye	.. Amm. Sulphate	2,00,000	70,000	34,100
		Amm. Phosph. Sulphate	1,35,000		
		Amm. Chloride	25,000		
		Superphosphate	44,710		
7.	Neyveli Lignite Corpn, Neyveli	.. Urea	1,54,000	70,000	—
8.	HSL, Rourkela	.. CAN	2,97,390	1,20,000	—
9.	Steel plants, by-product	.. Amm. Sulphate	81,800	16,860	—
10.	Superphosphate producers ..	.. Single Superphosphate	1,75,110	—	28,000
(b) Private Sector					
11.	EID-Parry, Ennore	.. Amm. Phosph. Sulphate	52,830		
		Amm. Sulphate	38,610	16,000	10,570
12.	Sahu Chemicals, Varanasi	.. Amm. Chloride	40,640	10,000	—
13.	GSFC, Baroda	.. Technical Grade Urea	3,500		
		Urea	1,00,000	96,000	50,000
		Ammonium Phos. Sulphate	2,56,000		
14.	Coromandel	.. Urea-phosphate	3,65,000		
		Urea	16,500	80,000	73,000
15.	DCM, Kota	.. Urea	2,40,000	1,30,000	—
16.	By-products from Coke-Ovens	.. Amm. Sulphate	48,020	9,890	—
17.	Superphosphate Producers ..	.. Single Superphosphate	11,08,000	—	1,77,260
18.	Dharamsi Morarji	.. TSP	27,000	—	12,150
B. FACTORIES UNDER IMPLEMENTATION					
(a) Public Sector					
1.	FCI, Durgapur	.. Urea	3,30,000	1,52,000	—
2.	FCI, Barauni	.. Urea	3,30,000	1,52,000	—
3.	FCI, Namrup Expansion ..	.. Urea	3,30,000	1,52,000	—
4.	FCI, Sindri Rationalisation	.. TSP	3,47,600	—	1,56,450
5.	FACT, Cochin	.. Urea	3,30,000	1,52,000	—
6.	FACT, Alwaye	.. Enrichment of present products	—	22,000	—
7.	Madras Fertilizers, Manali ..	.. Urea	2,10,000	1,90,000	85,000
		N-P-K Complex	3,60,000		
8.	IFFCO, Ahmedabad, Kandla Port	.. Urea	3,82,000		
		N-P-K	6,30,000	2,15,000	1,27,000
		Urea	2,64,000	1,20,000	—
9.	GSFC, Baroda	.. Urea	4,50,000	2,00,000	—
10.	IEL, Kanpur	.. Urea	50,000	—	8,110
11.	Superphosphate Producers ..	.. Superphosphate			

TABLE 9—LIST OF FERTILIZER PLANTS IN PRODUCTION, UNDER IMPLEMENTATION, LICENSED & PROPOSED (Contd.)

Sl. No.	Name of Factory	End Product	Annual capacity Te/yr.	Nutrient/year, Tonnes	
				N	P ₂ O ₅
C. FACTORIES LICENSED/LETTER OF INTENT					
(a) Public Sector					
1.	FCI, Trombay	To be decided	—	2,50,000	1,20,000
2.	FCI, Haldia	-do-	—	1,52,000	1,00,000
Other Public Sector					
1.	Hindustan Copper, Khetri	TSP	2,22,220	—	1,00,000
2.	Maharashtra Co-op., Thana	Amm. Chloride	66,000	16,500	—
Private Sector					
3.	Birla-Gwalior, Goa	Urea	3,40,000	1,60,000	—
4.	Malabar Chemicals, Mangalore	Urea	3,40,000	1,60,000	—
5.	EID, Parry	Amm. Chloride	60,000	15,000	—
6.	Dharamsi Morarji	DAP	5,00,000	90,000	2,39,000
7.	Birla, Mirzapur	Urea	3,40,000	1,60,000	—
8.	Occidental	To be decided	—	1,50,000	—
9.	Coromandel Expansion	-do-	—	1,50,000	55,000
10.	Kalinga Tube	Urea, N-P-K-Complex Fertilizers	—	2,26,000	85,000
11.	Maharashtra Agro Industries, Bombay	Superphosphate	48,000	—	7,680
D. FACTORIES PROPOSED					
1.	F.C.I., Ramagundam	Urea	4,95,000	2,28,000	—
2.	F.C.I., Talcher	Urea	4,95,000	2,28,000	—
3.	F.C.I., Nangal Expansion	Urea	3,30,000	1,52,000	—

[Planning Department, P & D Division, (FCI Ltd.) Sindri]
March '69

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EDITOR'S NOTE

It has been decided to publish in TECHNOLOGY research papers from scientists and technologists outside FCI Ltd. provided these are:

- (i) original and related to science and technology.
- (ii) approved by external referees chosen by the Editor, and
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The method of changing the chemistry of surface and geometry of pores developed earlier for silica has been applied on alumina and Florisil, using copper and sodium salts as modifying agents. By heating to 950°C, average pore radius of silica changed from 25 to 36 Å, of alumina from 32 to 133 Å, and that of Florisil from 31 to more than 5000 Å. Heating to the same temperature in presence of precoated salts resulted in 25 to 50 times faster elution for hydrocarbons (selectivity changing little in most cases and actually improving in a few cases) for alumina, whereas with Florisil the retention volumes dropped upto 6 times only for the saturated hydrocarbons, but actually increased for the aromatics. A significant change in retention characteristics was observed with sodium sulphate coated alumina when heated to different temperatures. Isolation and correlation of these textural and crystallochemical changes on adsorbent surface in terms of adsorbent parameters and gas-solid chromatographic properties, will result in tailor-made adsorbents for specific separations.

A method for finding gas hold-up in gas-solid chromatography has been proposed. An approximately linear relation was observed between the heats of adsorption of lower paraffins and surface areas of modified aluminas. Corrected retention volume per unit surface area for a hydrocarbon was found to vary widely for the modified adsorbents in this study, thereby indicating a difference in the distribution, energy content and nature of interactions of adsorption sites with methods of preparation, chemical nature, heat and salt treatments of the adsorbents.

Methods of Modification of Adsorbent Texture and Gas-Solid Chromatographic Properties

By SAMIR K. GHOSH, D. S. MATHUR AND N. C. SAHA,

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The utilities, potentialities and areas of excellence of gas-solid chromatography (GSC) over gas-liquid chromatography (GLC) have been discussed by many workers¹⁻⁹. However, efficient exploitation of GSC awaits improved adsorbents to meet these important properties among others, namely, uniformity in the distribution and energy content of adsorption sites, faster elution with symmetric peaks of large, polar and apolar sorbate molecules, longer linear range of adsorption isotherms, predictable selectivity from the consideration of structural features of sorbates and known parameters of sorbents. Considerable studies have been made on the modification of common adsorbents, alumina in particular, with a host of inorganic salts, and the result is a wide range of retention and selectivity for different types of sorbate molecules. But, a very few attempts have been made at isolation and correlation of retention volumes with various physico-chemical changes occurring on the adsorbent surface by salt-modification¹⁰⁻¹¹. These changes include solid-phase reaction between coating salts and exposed atoms and molecules on the adsorbent surface, thereby modifying its chemistry

as regards morphology, crystallinity, grain structure, alterations on the intricate three dimensional pore architecture (including tapering, constriction and tortuosity), and changes on the ionic nature and electron cluster of the adsorbent surface. Towards this end, the present study has been undertaken.

In a previous publication¹² Ghosh and Saha have observed drastic changes on the GSC characteristics of silica gel, by coating it with transition metal salts followed by heating to 950°C. Various factors of this modification affecting the gas-solid chromatographic properties of the adsorbents are under investigation in the authors' laboratory. The aim of the present investigation is to focus the impact of various changes of adsorbent surface upon GSC properties. Sawyer and Brookman¹⁰ have established that the functional groups of sorbate molecules contribute additively towards retention volumes. Projection of this finding on possible inter-adsorbent correlations based on elution behaviour and adsorbent parameters will constitute an important advance in GSC.

Experimental

An Aerograph 600D gas chromatograph with a flame ionization detector was used in this investigation, the carrier gas being Argon. The adsorbents were chromatographic grade alumina, active alumina, Florisil, and acid washed commercial silica gel. The characteristic details of heating and salt-modification of these sorbents were given in Table 1. Columns were packed in thoroughly cleaned and dried copper tubing of 1/8" or 1/4" OD. of different lengths by intermittent tapping with a rubber-padded glass rod. Heats of adsorption were determined gas chromatographically¹². Retention volumes were calculated from gas hold-up described in this paper.

Results and Discussion

(a) *Determination of Gas Hold-up*: No solute molecule is totally unadsorbed on gas-solid adsorbents. Therefore, the direct method of determination of gas hold-up is not applicable in GSC. It is proposed to determine gas hold-up from the extrapolated retention corresponding to zero carbon number, with the help of a plot of logarithm of uncorrected retention against carbon numbers of lower normal paraffins (Fig. 1). The C_0 -time has been observed to be smaller than the retention times of air, nitrogen and hydrogen when the GSC columns in Table 1 were tested in a Beckman GC-2A chromatograph fitted with a thermal conductivity detector.

Gas hold-up and retention volume (uncorrected for C_0 -time) of methane are given in Table 2 for a number

of columns. It is noted that both the parameters vary with the nature of adsorbents, their heat treatment and salt-modification. Taking gas hold-up volume as an index of column permeability (since columns were packed by a single worker under identical conditions as far as possible) some important observations follow. Comparing the gas hold-up volumes of columns 2, 3 and

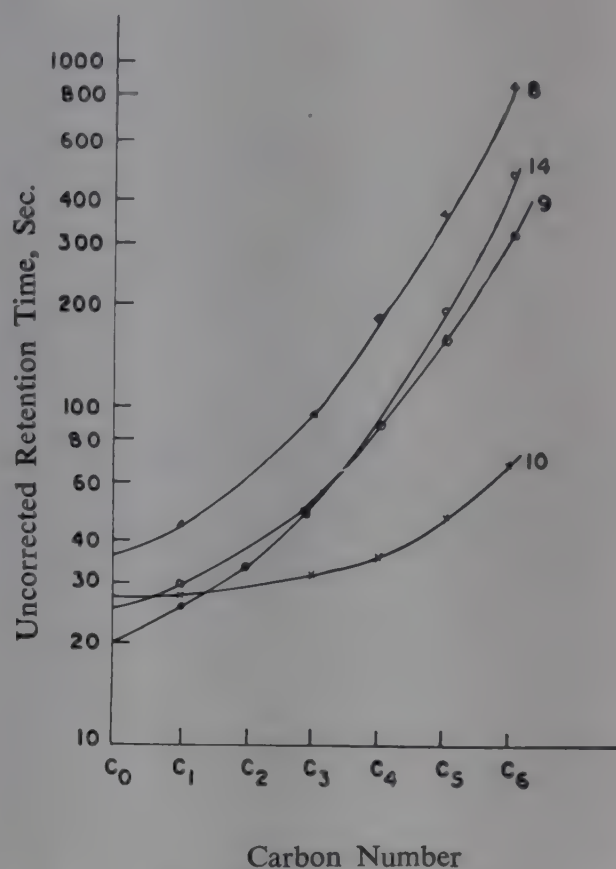


Fig. 1—Determination of Gas Hold-Up Time in Gas-Solid Chromatography

TABLE 1—DESCRIPTION OF GAS-SOLID ADSORPTION COLUMNS

Column No.	Column dimension	Adsorbent	Coating Salt	Heat treatment	
				Temp°C	Time, hrs
1.	3' × 1/8"	Chromatographic Alumina (B.D.H.) 100 mesh	Nil	200	4
2.	3' × 1/8"	"	Nil	950	7
3.	3' × 1/8"	"	Copper sulphate	950	7
4.	2' × 1/8"	"	Copper ammonium sulphate	950	7
5.	3' × 1/8"	"	Sodium sulphate	950	7
6.	5' × 1/8"	Silica 60/80 mesh	"	950	7
7.	10' × 1/8"	Active alumina 30/60 mesh	Nil	Nil	
8.	10' × 1/8"	"	Nil	950	3
9.	10' × 1/4"	"	Sodium sulphate	300	3
10.	10' × 1/4"	"	Sodium sulphate	950	3
11.	10' × 1/4"	Florisil (Hewlett Packward) 30/60 mesh	Nil	950	4
12.	10' × 1/4"	"	Copper sulphate	950	4
13.	3' × 1/8"	Silica 60/80 mesh	Nil	950	7
14.	10' × 1/8"	Active alumina 30/60 mesh	Nil	300	3

TABLE 2—CHANGES IN THE GAS HOLD-UP AND METHANE RETENTION VOLUMES WITH ADSORBENT MODIFICATION

Column No.	Column Material	Column tem.°C	Gas Hold-up Vol. ml./g.	Uncorrected Methane Retention Vol. ml./g.
2.	BDH, Al ₂ O ₃ , heated 950°C	80	2.6	16.1
3.	BDH, Al ₂ O ₃ -CuSO ₄ , heated 950°C	80	1.3	3.2
5.	BDH, Al ₂ O ₃ -Na ₂ SO ₄ , heated 950°C	80	2.9	12.8
6.	Silica-Na ₂ SO ₄ , heated 950°C	80	2.9	3.4
8.	Active alumina, heated 950°C	180	2.6	3.7
9.	Active alumina-Na ₂ SO ₄ , heated 300°C	200	1.8	2.1
10.	Active alumina-Na ₂ SO ₄ , heated 950°C	200	0.9	1.0

5 in Table 2 it is noted that alumina becomes more permeable than the blank when treated with sodium sulphate but less permeable than the blank when modified with copper sulphate. A large effect on permeability by heating of the sodium sulphate modified alumina is observed in columns 9 and 10. Permeability is also strongly dependent on the starting material (compare the results for BDH and active alumina in Table 2). These changes were caused by alterations in the void space in the interstices as well as in the intraparticle pores. Visible indications of changed flow resistance were noticed from the appreciable amount of shrinkage of the adsorbents by heating and salt-modification.

(b) *Adsorbent Texture and Heats of Adsorption:* The methods of crystallo-chemical and geometrical modification of silica, established in this laboratory¹² were applied on other adsorbents in this investigation. The various textural changes and heats of adsorption of propane, n-butane and n-pentane are given in Table 3.

The large decrease in specific surface of alumina from 152 to 44 m²/g. by heating at 950°C in air as compared to the corresponding meagre change in silica¹² from 375 to 296 m²/g is due to the sintering of the micropores of alumina. The simultaneous increase in pore volume is indicative of further widening of the existing big pores in alumina. That the anion or ligand of modifying salts affects the pore geometry of alumina is evident from the comparison of results of copper sulphate and copper-ammonium sulphate in columns 3 and 4. Similarly, a strong cationic effect is observed in columns 3 and 5 (0.173 g. sulphate ion/g. of adsorbent being used in both the cases) where copper caused more severe alteration in the texture of alumina than sodium. But the reverse is true with silica gel as can be seen by comparing the support material in column 6 with a copper sulphate modified silica of specific surface 24 m²/g, pore volume 0.477 ml/g. and mean pore radius, 398Å (from Table 1 of reference 12). Comparing the results of columns 2

TABLE 3—CHANGES IN THE TEXTURE AND HEATS OF ADSORPTION WITH HEAT TREATMENT AND SALT-MODIFICATION OF ADSORBENTS

Column No.	Adsorbent	Texture			ΔH , K.cal/mole		
		Surface area, m ² /g.	Pore volume, ml./g.	Avg. pore radius Å	Propane	n-Butane	n-pentane
1.	B.D.H. Al ₂ O ₃	152	0.242	32	3.8	5.5	6.8
2.	B.D.H. Al ₂ O ₃ , heated 950°C 7 hours.	44	0.295	133	2.2	3.5	4.5
3.	B.D.H. Al ₂ O ₃ -CuSO ₄ , heated 950°C	7.2	0.272	761	1.6	2.7	3.5
4.	B.D.H. Al ₂ O ₃ -Cu(NH ₃) ₄ SO ₄ heated 950°C	11.4	0.291	511	1.7	2.8	3.7
5.	B.D.H. Al ₂ O ₃ -Na ₂ SO ₄ , heated 950°C	42.0	0.171	81	2.1	3.3	4.2
6.	SiO ₂ -Na ₂ SO ₄ , heated 950°C	1.5	0.123	1640	1.8	3.0	4.5
7.	Active Alumina, heated 950°C	242	0.271	22	—	—	—
8.	Active Al ₂ O ₃ -Na ₂ SO ₄ , heated 950°C	57	0.291	102	—	—	—
9.	Florisil heated 950°C	1.5	0.393	5,240	—	—	—
10.	Florisil CuSO ₄ , heated 950°C	0.15	0.338	44,400	—	—	—
11.	SiO ₂ , heated 950°C	296	0.545	36	—	—	—

and 5 with those of columns 6 and 13 in Table 3 a more drastic texture-change by sodium sulphate modification is noticed on silica than on alumina; most of the pores in silica were blocked, whilst those in alumina underwent only mild change, with pore volume being reduced to half.

Obviously, the mechanism of textural change by salt-modification differs greatly with the nature of adsorbents. Incidentally, Mougey Francois-Rossetti and Imelik¹⁴ have reported that a silica gel (of surface area 695 m²/g, pore volume 0.50 ml/g, $22\text{\AA} < r_p < 70\text{\AA}$ = 17%) when heated to 150°C in vacuo with 1.50×10^{-3} Na⁺/g underwent a significant change in pore geometry. (specific surface 380 m²/g, pore volume 0.35 ml/g, $22\text{\AA} < r_p < 70\text{\AA}$ = 55 per cent).

Kiselev¹⁵ has proposed a theory of grain swelling in order to explain the large pore-widening of silica gels produced by steam-heating under pressure. Electron microphotos have confirmed that big pores were generated by grain-swelling in the modified adsorbents in Table 1 and the results will be published soon¹³. However, mention may be made that there is no theory dealing directly with the mechanism of textural change of adsorbents by heating in presence of coated salts. A co-precipitate of silica and magnesia, commercially known as Florisil when heated at 950°C in air revealed a drastic change in texture (vide column 11 in Table 3). According to Snyder¹⁶ the uncalcined Florisil of 298 m²/g specific surface, 0.461 ml/g. pore volume and 31Å average pore radius could be reduced to a specific surface, as low as 155 m²/g when heated at 400°C in air.

The heats of adsorption of propane, n-butane and n-pentane seem to bear a somewhat linear relation with specific surfaces of modified aluminas (Fig. 2). An examination of the results of columns 5 and 6 in Table 3 reveals very little change in the heats of adsorption on silica and alumina when both are modified identically with sodium sulphate, although the latter support has 20 times larger mean pore radius.

An approximately linear variation of ΔH against carbon number of lower normal paraffins was observed in Fig. 3 for the modified aluminas. Keibel et al¹⁷ have made the same observation with steam heated macroporous silicas.

Kiselev et al¹⁸ have reported differential heats of adsorption for propane from 7.9 to 5.2 K. Cal/mole for silica gels of pore diameters from 32 to 1700 Å. Comparing their results with those of modified aluminas (Table 3), which show the range of heats of adsorption for propane from 1.6 to 3.8, a much faster elution power

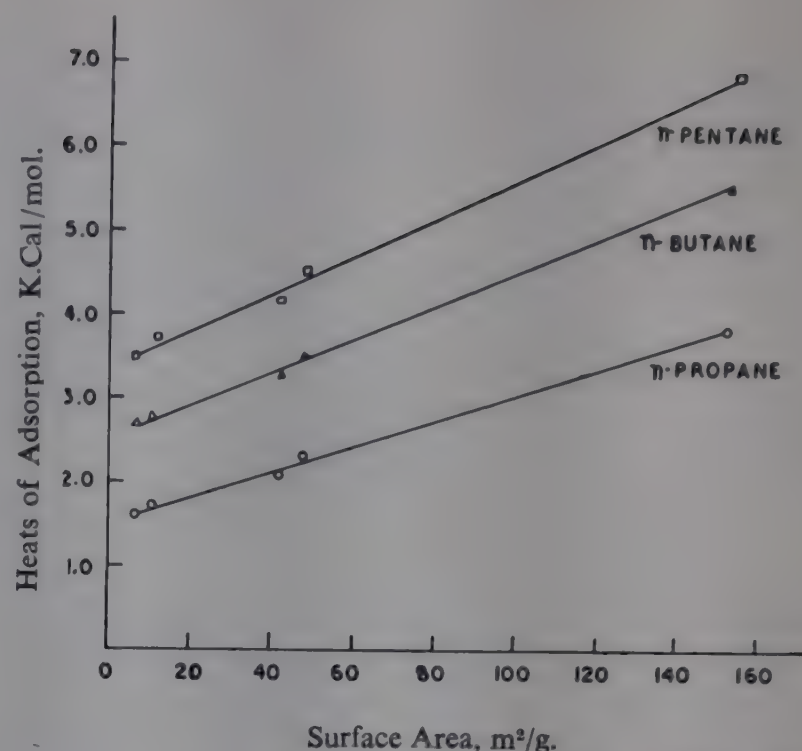


Fig. 2—Correlation of Heats of Adsorption of Lower Paraffins and Surface Areas of Modified Aluminas

(and hence speedier analysis) is possible with aluminas than with silicas¹⁸ of comparable pore diameters. Moreover, their data give an approximately linear variation of ΔH against logarithm of mean pore diameter squared, whilst our data on modified aluminas fit into a curve (Fig. 4).

(c) *Elution Characteristics:* Specific retention volumes of modified aluminas, silicas and Florisil are given in Table 4A. for three paraffins. Comparing the results

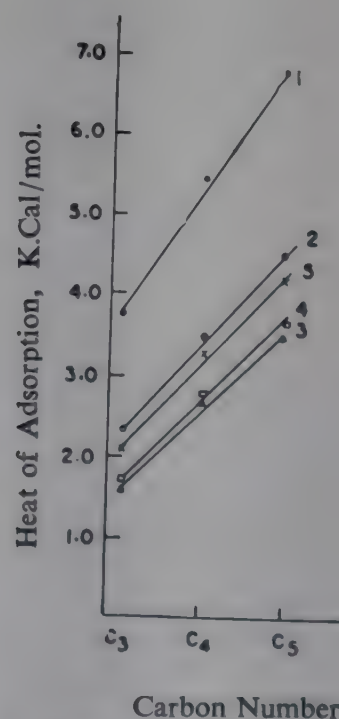


Fig. 3—Linearity of Carbon Numbers of Normal Paraffins and their Heats of Adsorption from Aluminas

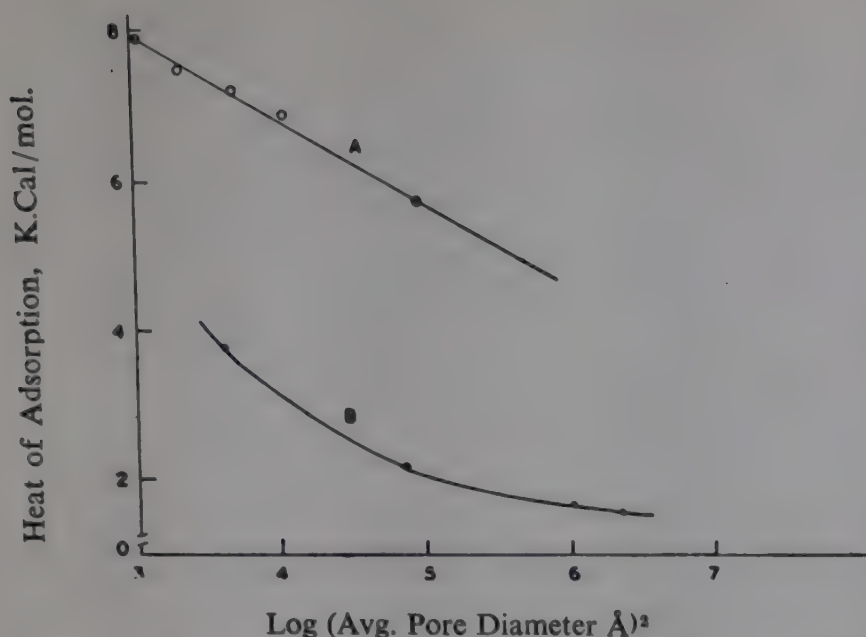


Fig. 4—Nature of Variation of Heats of Adsorption of n-Propane and Mean Pore Diameter Squared for Kiselev's Steam-Heated Silicas and our Modified Aluminas

of columns 1 and 2 at 100°C it is noted that the elution power of alumina is improved from 1.4 to 3.5 times by heating to 950°C. The effect of heat-treatment and salt-modification of alumina on elution power and speed of analysis can be better seen from Table 4B.

TABLE 4A—CHANGES IN THE SPECIFIC RETENTION VOLUMES OF LOWER ALKANES WITH MODIFICATION OF ADSORBENTS

Column No.	Temperature °C	Propane	V _g , ml/g. of n-Butane	n-Pentane
1.	100	1.21	3.70	9.87
2.	100	0.88	1.55	2.96
3.	100	0.04	0.06	0.11
4.	100	0.44	0.61	1.02
5.	100	0.42	0.64	1.05
6.	100	0.11	0.14	0.17
8.	200	1.40	2.93	10.05
9.	200	0.41	0.92	1.29
10.	200	0.05	0.08	0.09
11.	140	—	—	0.06
12.	140	—	—	0.29

TABLE 4B—EFFECT OF MODIFICATION OF ALUMINA ON SPEED OF ANALYSIS

Column No.	Modification	Comparative elution time at 100°C for		
		Propane	n-Butane	n-Pentane
1.	Nil	100	100	100
2.	Heated to 950°C	72.7	41.9	30.0
3.	Copper sulphate	3.3	1.6	1.1
4.	Copper ammonium sulphate	36.4	16.5	10.3
5.	Sodium Sulphate	34.7	17.3	16.1

In Table 5 the relative retention of n-pentane for both columns are taken as unity, but, their absolute values are 2.96 and 0.11 ml/g at 100°C for heated and copper-sulphate treated alumina respectively. Since copper-sulphate treated alumina represents the fastest column it is relevant and interesting to compare the selectivity of this and heated-alumina column towards different types of sorbate molecules (Table 5). Relative to n-pentane other normal alkanes, especially, the higher homologues, are retarded much more in column 3 than in column 2. Similarly, olefins and cycloparaffins are somewhat retarded more in column 3 than in column 2. Relative retentions of simpler isoparaffins are slightly larger and of more branched ones are much lower in heated alumina than in copper sulphate modified alumina. Most spectacular change in the elution behaviour is the irreversible adsorption of aromatics by column 3, whereas benzene and toluene were eluted from column 2 although with much larger retardation as compared with corresponding saturated hydrocarbons.

By converting the retention volume in Table 4A from ml./g. to ml./unit surface area of adsorbents a wide variation in values results, thereby implying a big change in the distribution and energy content of adsorption sites (i.e. the retentive forces in GSC) with their chemical nature, heat and salt modifications.

TABLE 5—COMPARATIVE SELECTIVITY TOWARDS ISOMETRIC HYDROCARBONS FROM ALUMINA AND COPPER SULPHATE MODIFIED ALUMINA COLUMNS

Compound	Relative Retention at 100°C	
	B.D.H. Al ₂ O ₃ Column No. 2	B.D.H. Al ₂ O ₃ -CuSO ₄ Column No. 3
Ethane	0.31	0.41
Ethylene	0.34	0.39
n-Pentane	1.00	1.00
Pentene-1	1.55	1.74
n-Hexane	1.93	2.13
Cyclohexane	1.79	1.68
Benzene	6.49	No elution
Methylcyclopentane	1.73	1.68
2-Methylpentane	1.72	1.70
n-Heptane	4.20	5.00
Methylcyclohexane	3.37	3.67
2,4-Dimethylpentane	3.14	3.02
n-Octane	5.45	13.78
1-trans 2-Dimethylcyclohexane	6.45	7.76
1-cis 2-Dimethylcyclohexane	6.46	7.50
2,2,4-Trimethylpentane	4.89	5.53

(d) *Modification of Florisil and Selectivity of C₆-Hydrocarbons*: Retention data of blank and copper sulphate treated Florisil for four C₆-hydrocarbons of different types are given in Table 6. Comparison of results of columns 11 and 12 reveals 3 to 5 times higher retention for normal and cyclo-hexane by the salt-treated Florisil. This is just opposite to the results obtained with alumina and silica. This might be due to a different type of chemical reaction of copper sulphate with Florisil surface, causing an entirely different retentive mechanism. Considering the fact that the copper sulphate modified Florisil has tenth of the surface area of the blank and is accompanied by a slight change in pore volume (thereby widening the mean pore radius about 8 times) several times faster elution of saturated hydrocarbons was expected from the salt-treated adsorbent. Salt-modification of Florisil at temperatures lower than 950°C where sintering will be much less, is likely to give interesting results. Mention may be made that Florisil turned blue, while alumina and silica changed from grey to black under similar modification with copper sulphate. Another significant difference in elution property is the retention of benzene which is reduced to half on copper sulphate modified Florisil and is completely subtracted in similarly treated alumina.

(e) *Effect of Heating of Salt-coated Adsorbents*: It is evident from the discussion so far that any textural change of adsorbent is well reflected in its GSC behaviour. However, an important aspect which seems to have been very scantily investigated, is the nature and extent of change in the retention characteristics of adsorbents, whose surface has been subjected to solid-phase reaction with respect to morphology, crystallinity, formation of solid-solution etc. Differential thermal analysis (DTA) of the adsorbents can be taken as a fair indication of these changes, as can be seen from Figs 5 and 6 for alumina and salt modified alumina and silica.

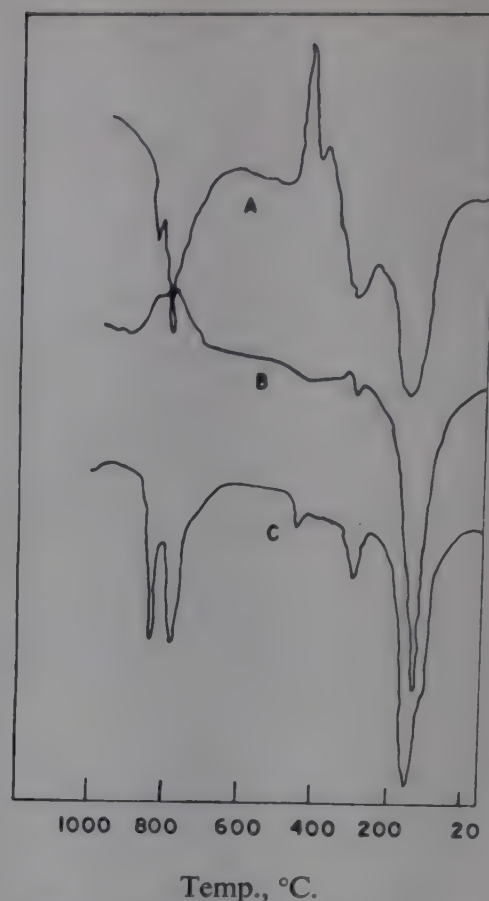


Fig. 5—Differential Thermograms

A—Alumina Coated with Copper Ammonium Sulphate
B—Untreated Alumina
C—Alumina Coated with Copper Sulphate

For studying this phenomenon a thermally stable coating salt on the adsorbent is preferable. In this investigation two columns containing equal amounts of sodium sulphate on active alumina, one heated to 300°C, the other to 950°C for 3 hours in air were chosen. The DTA curve D in Fig. 6 shows changes corresponding to these two temperatures. Moreover, sodium sulphate itself is known to have several polymorphic forms¹⁹ in this temperature zone.

The elution characteristics at two temperatures of four C₆-hydrocarbons from these two columns as well as

TABLE 6—CHANGES IN THE RETENTION CHARACTERISTICS OF SOME C₆-HYDROCARBONS WITH MODIFICATION OF FLORISIL BY COPPER SULPHATE

Compound	Column No. 11, Florisil heated 950°C				Column No. 12, Florisil-CuSO ₄ heated 950°C			
	140°C		160°C		140°C		160°C	
	Vg ml./g	Relative Retention	Vg ml./g	Relative Retention	Vg ml./g	Relative Retention	Vg ml./g	Relative Retention
n-Hexane	0.10	1.00	0.06	1.00	0.30	1.00	0.28	1.00
Cyclohexane	0.09	0.90	0.06	1.00	0.30	1.00	0.27	0.96
Cyclohexene	0.28	2.80	0.15	2.50	0.33	1.10	0.30	1.07
Benzene	1.02	10.20	0.54	9.00	0.43	1.43	0.34	1.21

from their blanks were given in Table 7. Column 10 represents about ten times faster elution than column 9, but the predominant cause is the textural change of alumina by heating from 300°C to 950°C, as can be seen by comparing the results from these columns with those from the corresponding blanks. It is implied that a clear demonstration of the effect of reaction between adsorbent surface and coating salt (brought about by heating) necessitates an adsorbent which does not undergo much textural change by heating. For example, a silica gel was found to change in average pore diameter from 25Å to 36Å by heating from 200°C to 950°C.

However, the effect of solid-phase reaction of sodium sulphate and alumina is clearly indicated by the differential selectivities of cyclohexene and benzene. For example, the ratio of relative retention volumes of cyclohexene at 180°C in columns 10 and 8 is 2.13/1.51

TABLE 7—CHANGES IN THE GAS CHROMATOGRAPHIC PROPERTIES OF SOME ISOMERIC HYDROCARBONS WITH HEAT TREATMENT OF ALUMINA-SODIUM SULPHATE ADSORBENT

Compound	180°C		200°C	
	Vg. ml./g.	Relative Retention	Vg. ml./g.	Relative Retention
(A) Column No. 8, Al ₂ O ₃ , 950°C.				
n-Hexane	2.39	1.00	2.00	1.00
Cyclohexane	2.12	0.88	1.71	0.86
Cyclohexene	3.60	1.51	2.82	1.41
Benzene	7.05	2.95	5.08	2.54
(B) Column No. 10. Al ₂ O ₃ -Na ₂ SO ₄ , 950°C				
n-Hexane	0.60	1.00	0.30	1.00
Cyclohexane	0.51	0.85	0.23	0.76
Cyclohexene	1.28	2.13	0.53	1.76
Benzene	3.00	4.99	1.10	3.66
(C) Column No. 14 Al ₂ O ₃ , 300°C				
n-Hexane	31.33	1.00	24.32	1.00
Cyclohexane	26.81	0.84	20.78	0.85
Cyclohexene	45.76	1.44	33.77	1.38
Benzene	—	—	63.94	2.63
(D) Column No. 9 Al ₂ O ₃ -Na ₂ SO ₄ , 300°C				
n-Hexane	6.99	1.00	3.97	1.00
Cyclohexane	6.14	0.87	3.62	0.96
Cyclohexene	10.89	1.55	5.90	1.48
Benzene	23.14	3.31	12.82	3.23

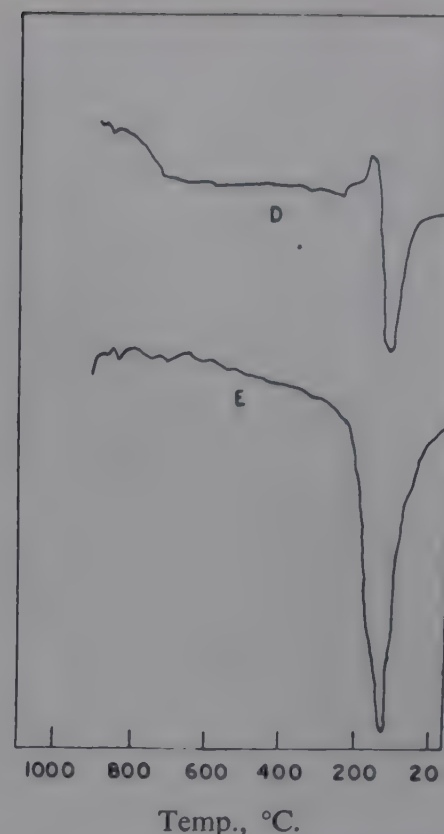


Fig. 6—Differential Thermograms
D—Alumina Coated with Sodium Sulphate
E—Silica Coated with Sodium Sulphate

and in columns 9 and 14 is 1.55/1.44; the corresponding ratios for benzene at 200°C are 3.66/2.54 and 3.23/2.63 respectively. Mention may be made that cyclohexane was retained almost equally (relative to n-hexane) in all the four columns.

Among other notable differences in the chromatographic properties of the two sodium sulphate modified columns are the values of

$$\{(Vg)_{\text{Column 8}} - (Vg)_{\text{Column 10}}\} \text{ and } \{(Vg)_{\text{Column 9}} - (Vg)_{\text{Column 14}}\}$$

and the temperature coefficient of selectivity towards unsaturated hydrocarbons. In passing from 200°C to 180°C the ratio of relative retention changes from 1.2 to 1.05 for cyclohexene and from 1.36 to 1.03 for benzene when the results of column 10 are compared with those of column 9. These effects are also associated with the change in chemical nature of the surface of Al₂O₃-Na₂SO₄ when heated at 300°C and 950°C before packing in the column.

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Solubilities of dicalcium phosphate dihydrate ($\text{CaH PO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrous dicalcium phosphate (CaHPO_4) have been determined in ammonium sulphate and ammonium nitrate solutions of various concentrations at 35°C . These increase with the increase in ammonium sulphate concentration. In any particular concentration of ammonium sulphate, dicalcium phosphate dihydrate is more soluble than anhydrous dicalcium phosphate. The solubility in ammonium sulphate solution of a particular concentration decreases when ammonium nitrate is also present.

Solubilities of Dicalcium Phosphate Dihydrate and Anhydrous Dicalcium Phosphate in Ammonium Sulphate and Ammonium Nitrate Solutions

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Different soluble nitrogenous compounds are known to have different effects on the solubility and availability of phosphates in fertilizers¹. References^{2,3} have been made on the increase in solubility of dicalcium phosphate in ammonium sulphate solution but detailed data are not available. Since dicalcium phosphate is a major constituent of nitrophosphates and many other mixed

N-P and N-P-K fertilizers, a systematic study of its solubility in presence of ammonium sulphate and such other nitrogenous compounds would be useful.

In this paper, the results of determination of solubilities of dicalcium phosphate, both anhydrous and hydrated, in ammonium sulphate solutions of different concentrations are reported. Some experimental data

are also given on the solubility of dicalcium phosphate in presence of (a) ammonium nitrate (b) mixtures of ammonium sulphate and ammonium nitrate and (c) mixtures of ammonium sulphate, ammonium nitrate and calcium carbonate.

Experimental

Materials & Equipment: All solutions were made in deionized carbon dioxide-free conductivity water; the chemicals used were of A. R. or G. R. quality.

The apparatus (Fig. 1) used is the same described before⁴. It is suitably designed for solubility studies in which equilibrium concentrations are likely to be affected due to possible leakage of gaseous component. The apparatus can be placed inside a thermostat for carrying out experiments at constant temperatures, and the use of an internal stirrer is eliminated. An arrangement is made for the rotation of the apparatus by an A. C. motor.

Procedure: In determining the solubilities of dicalcium phosphate in different concentrations of ammonium sulphate solutions, excess of solid dicalcium phosphate was kept in contact with the ammonium sulphate solution of a particular concentration. Samples of the liquid above the solid were taken out at different intervals of time and analysed until a constant value was attained.

The liquid sample was analysed for calcium, sulphate, phosphate and nitrogen (ammoniacal). For the estimation of calcium in the presence of phosphate, precipitation of calcium oxalate was made from an acetic acid medium and then calcium was determined in the usual way by titration against a standard solution of potassium permanganate⁵. Sulphate analyses were performed using the standard gravimetric method⁵. All estimations of phosphate were carried out by the colorimetric molybdo-vanado-phosphate method using a spectronic-20 colorimeter⁶. Nitrogen was estimated by the standard AOAC method⁷ by Kjeldahl distillation.

The anhydrous dicalcium phosphate used in these studies was prepared in the laboratory according to the method of Comstock et al⁸. It consists of precipitating anhydrous dicalcium phosphate by adding diammonium phosphate (A.R.) (0.88 m) solution to (A.R.) calcium chloride (0.88 m) solution kept in a wide mouthed round bottomed flask. The solutions of diammonium phosphate and calcium chloride were first kept separately in a constant temperature water bath ($\pm 0.01^\circ\text{C}$) to attain a temperature of 80°C ; then the diammonium phosphate solution was added to the calcium chloride solution at a rate of 90 ml./min. During precipitation, the contents of the flask were vigorously stirred and the precipitation was stopped when the pH became 5.0. The resultant precipitate was filtered, washed with deionized water till free from chloride ions and dried at $110\text{--}120^\circ\text{C}$ to a constant weight. The sample prepared had the following characteristics: calcium and P_2O_5 contents were 29.4 and 50.9 per cent respectively; on heating upto $250\text{--}270^\circ\text{C}$ no moisture was given out.

The above results showed that the sample prepared in the laboratory was anhydrous dicalcium phosphate, which was also confirmed by x-ray diffraction analysis. The hydrated dicalcium phosphate used in the present studies was confirmed to be dicalcium phosphate dihydrate ($\text{Ca HPO}_4 \cdot 2\text{H}_2\text{O}$) by x-ray diffraction method.

Results and Discussion

It will be observed from the results (Table 1) that the solubility of dicalcium phosphate dihydrate in presence of ammonium sulphate goes on increasing with the

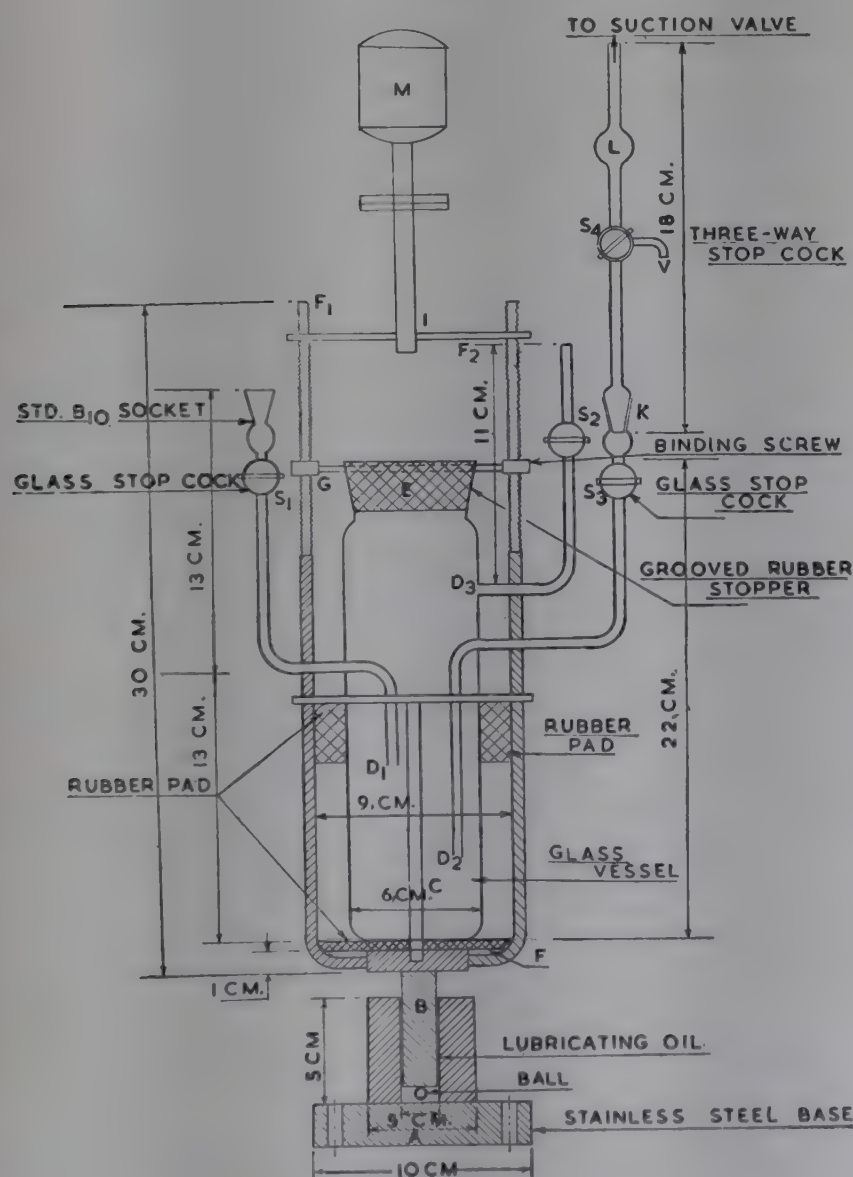


TABLE 1—EFFECT OF AMMONIUM SULPHATE SOLUTION ON THE SOLUBILITY OF DICALCIUM PHOSPHATE DIHYDRATE

(at 35°C)

(NH ₄) ₂ SO ₄ , w/w %	Time days	g./100g. of Soln.			
		P ₂ O ₅	SO ₄	Ca	N
0	4	0.008	—	0.005	—
5	1	0.070	3.612	0.046	1.031
	2	0.072	3.582	0.039	1.031
	3	0.079	3.612	0.040	1.024
10	1	0.112	7.260	0.073	2.113
	2	0.121	7.186	0.067	2.152
	3	0.121	7.198	0.074	2.152
15	1	0.166	10.820	0.086	3.154
	2	0.168	10.620	0.088	3.172
	3	0.174	10.572	0.087	3.181
20	1	0.212	14.028	0.121	4.146
	2	0.217	13.686	0.126	3.982
	3	0.228	13.620	0.130	3.854
25	1	0.284	17.904	0.133	4.951
	2	0.303	17.736	0.139	4.920
	3	0.324	17.220	0.140	5.002
30	1	0.366	20.758	0.145	6.113
	2	0.368	20.700	0.148	6.104
	3	0.415	20.700	0.153	5.961
35	1	0.484	24.048	0.150	7.050
	2	0.515	23.986	0.153	6.943
	3	0.530	23.952	0.154	6.920

increase in ammonium sulphate content of the solution. The saturated solution of dicalcium phosphate in various concentrations of ammonium sulphate solution were analysed for phosphate, sulphate, calcium and nitrogen content. It will be seen that P₂O₅ content of the solution goes on increasing with increase in ammonium sulphate concentration (from 0.075 g./100 g. of soln. in 5 per cent ammonium sulphate to 0.53 g./100 g. of solution in 35 per cent ammonium sulphate solution). There is also an increase in the concentration of calcium ions in the solution with the increase in ammonium sulphate concentration. But the ratios of concentration of phosphate ions and calcium ions found are not exactly the same as in dicalcium phosphate dihydrate; the concentration of calcium ions is somewhat less. This may be due to the formation of insoluble calcium sulphate since there is also a decrease in the sulphate content. At higher concentration of ammonium sulphate there is also some decrease in the nitrogen content of the solu-

tion; this may be due to the formation of a double salt of calcium sulphate and ammonium sulphate.

In most of the nitric phosphates dicalcium phosphate is present along with ammonium nitrate. Hence, a study was made on the solubility of dicalcium phosphate dihydrate in pure ammonium nitrate solutions as well as in a solution containing both ammonium nitrate and ammonium sulphate. The results of these studies (Table 2) show that the solubilizing effect of ammonium nitrate on dicalcium phosphate dihydrate is much less than that of ammonium sulphate. The solubility of dicalcium phosphate dihydrate in a mixture of ammonium sulphate and ammonium nitrate is somewhat less but of the same order as that in pure ammonium sulphate solution. Hence, the presence of ammonium nitrate in a fertilizer does not have much effect on the solubility of dicalcium phosphate dihydrate in ammonium sulphate.

TABLE 2—EFFECT OF AMMONIUM SULPHATE AND AMMONIUM NITRATE SOLUTIONS ON THE SOLUBILITY OF DICALCIUM PHOSPHATE DIHYDRATE AT 35°C.

[At equilibrium]

(NH ₄) ₂ SO ₄ , w/w %	NH ₄ NO ₃ , w/w %	g./100g. Soln.	
		P ₂ O ₅	Ca
0	10	0.047	0.031
	20	0.065	0.042
	25	0.072	0.045
	30	0.073	0.048
10	10	0.122	0.070
	20	0.130	0.073
	25	0.132	0.073
	30	0.130	0.072
15	10	0.161	0.095
	20	0.158	0.095
	25	0.155	0.091
	30	0.150	0.090
20	10	0.220	0.105
	20	0.218	0.098
	25	0.215	0.093
	30	0.211	0.093
25	10	0.312	0.113
	20	0.304	0.105
	25	0.300	0.100
	30	0.300	0.100
30	10	0.408	0.102
	20	0.413	0.092
	25	0.421	0.072
	30	0.420	0.060

In Table 3 are given the solubilities of dicalcium phosphate dihydrate in ammonium sulphate solutions of varied concentrations in presence of different amounts of ammonium nitrate and calcium carbonate which are commonly found together in some mixed fertilizers. It is seen that the solubility of dicalcium phosphate dihydrate in ammonium sulphate solution actually shows some decrease when either or both of ammonium nitrate and calcium carbonate are present along with ammonium sulphate.

TABLE 3—EFFECT OF AMMONIUM SULPHATE, AMMONIUM NITRATE AND CALCIUM CARBONATE ON THE SOLUBILITY OF DICALCIUM PHOSPHATE DIHYDRATE AT 35°C

[At equilibrium]				
(NH ₄) ₂ SO ₄ w/w%	NH ₄ NO ₃ w/w%	CaCO ₃ w/w%	g./100g. Soln	
			P ₂ O ₅	Ca
10	10.09	1.410	0.100	0.080
	0	1.087	0.098	0.072
15	14.99	1.262	0.135	0.192
	0	1.004	0.151	0.101
20	19.93	1.082	0.198	0.085
	0	1.074	0.210	0.121
25	24.90	1.204	0.287	0.092
	0	0.861	0.295	0.138
30	30.04	0.980	0.226	0.090
	0	0.930	0.308	0.141

In Table 4 are given the results of solubility determination of anhydrous dicalcium phosphate in pure ammonium sulphate solution of different concentrations. It will be observed that here also the solubility increases with the increase in the concentration of ammonium sulphate solutions (from 0.06 to 0.224 g./100 gm. of solution) as in the case of dicalcium phosphate dihydrate. But by comparing these results with those in Table 1, it will be seen that the solubility at a particular concentration of ammonium sulphate solution of anhydrous salt is much smaller than that of hydrated dicalcium phosphate.

It is also clear from these results that when dicalcium phosphate dihydrate in a suitable proportion is used in a fertilizer mixture along with ammonium sulphate, a considerable portion of the phosphate will be rendered water-soluble and quickly available to plant. This effect will be lower when anhydrous dicalcium phosphate is used.

TABLE 4—EFFECT OF AMMONIUM SULPHATE SOLUTION ON THE SOLUBILITY OF DICALCIUM PHOSPHATE (ANHYDROUS) AT 35°C

of (NH ₄) ₂ SO ₄ w/w%	Time, days	g./100g. Soln.			
		P ₂ O ₅	SO ₄	Ca	N
0	4	0.007	—	0.004	—
5	2	0.052	3.598	0.030	1.042
	3	0.064	3.564	0.030	1.020
10	2	0.104	7.008	0.043	2.051
	3	0.113	6.984	0.045	2.033
15	2	0.126	10.418	0.055	3.041
	3	0.126	10.368	0.062	3.022
20	2	0.141	14.026	0.062	4.106
	3	0.142	13.964	0.067	4.064
25	2	0.162	17.290	0.095	5.007
	3	0.165	17.220	0.085	4.912
30	2	0.184	21.031	0.072	6.220
	3	0.220	20.548	0.082	6.208

Dicalcium phosphate in mixed and compound fertilizers is commonly regarded as water-insoluble, since it shows a low value of water-solubility by the standard AOAC method, but when it is present along with ammonium sulphate, its solubility will be high when water-solubility is determined by the same procedure, as is evident from the results (Tables 1 and 4). Hence, in many mixed fertilizers, containing ammonium sulphate and dicalcium phosphate, the latter will also contribute water-solubility to some extent.

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The influence of growing wheat crops on the numerical abundance of ureolytic and nitrate-reducing bacteria has been studied. The rhizosphere and rhizoplane have been found to harbour a higher bacterial population. The degree of increase in case of ureolytic bacteria is quite spectacular and is many times higher than that of total and nitrate-reducing bacteria. The important role played by the increased bacterial population in the nitrogen economy of the soil has been discussed.

Abundance of Ureolytic and Nitrate-Reducing Bacteria in the Rhizosphere of Wheat

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The earlier communications¹⁻³ from this laboratory have shown that urea is hydrolysed into ammonia and carbon dioxide within a few days after its application into the soil, and the chief agents responsible for the hydrolysis are soil micro-organisms of which bacteria playing the most important role. Ammonia, thus released into the soil, is further acted upon by the nitrifying bacteria resulting in the accumulation of nitrite and nitrate, which are easily leached by field water into the deeper layers of soil where they are reduced by denitrifying bacteria mostly to gaseous nitrogen in the prevalent anaerobic environment.

Thus, it is evident that the ureolytic bacteria and nitrate-reducers are directly connected with the nitrogen economy of soil. Hence, it was felt necessary that a study should be undertaken to determine the influence of growing crops on the numerical abundance of these groups of bacteria in soils and rhizosphere of crop plants.

Material and Methods

Wheat variety *Sonora 64* was grown in plots in Nov. 1968. Root and soil samples were collected after about a month of sowing, and analysed for the bacterial population on the very day of collection. Soil from unsown plots served as control.

Soil adhering loosely to roots was removed and the roots with the rhizosphere soil were put into 180 ml. of sterile distilled water in flask. After a thorough shaking, the roots were taken out aseptically. The

amount of soil added to the water was determined by weighing the flask before the addition of the roots associated with soil and again after the removal of the washed roots. This was used as the basic suspension from which serial dilutions were made.

For the analysis of rhizoplane bacteria roots, from which rhizosphere soil had been removed, were used. These were then washed thoroughly in several changes of sterile distilled water, the excess water was then removed from the roots by blotting them against sterile filter papers. A known amount of root was then crushed in a sterile mortar and pestle aseptically and serial dilutions were made in the usual manner. A part of the root or soil samples were used for the determination of their moisture contents by drying in oven at 100°C.

1 ml. aliquots from appropriate dilutions of rhizosphere and control soils and the crushed root suspension were planted in quintuplicate in tubes of suitable media. For total bacteria, nutrient broth was used. Nitrate-reducers were cultured in a nitrate broth in accordance with the standard method⁴ and the presence of ureolytic bacteria was detected in the medium proposed by Das and Khan¹. For the enumeration of total, ureolytic and nitrate-reducing bacteria the most probable number method⁵ was employed. Readings were taken after 6 days of incubation at 30°C.

Results and Discussion

The numerical assessment of bacteria capable of hydrolysing urea and reducing nitrate has been made in

a number of experiments and the representative results are given in Table 1.

TABLE 1—EFFECT OF GROWING ROOTS ON THE ABUNDANCE OF UREOLYTIC AND NITRATE-REDUCING BACTERIA

[Numbers in millions/g. oven-dry material]					
	Control Soil	Rhizo- sphere	*R:C	Rhizo- plane	Rp†:C
Total bacteria	18.1	598.2	33.0	7894	436
Ureolytic bacteria	0.288	29.9	103.9	2512	8722
Nitrate Reducers	3.52	17.9	5.1	7894	224

$$*R:C = \frac{\text{numbers in rhizosphere soil}}{\text{numbers in control soil}}$$

$$†Rp:C = \frac{\text{numbers in rhizoplane}}{\text{numbers in control soil}}$$

From the data (Table 1) it is evident that rhizosphere soil and rhizoplane (root surface) have sustained higher bacterial population. This is true not only for total bacteria but also in case of ureolytic bacteria and nitrate reducers. The degree of increase, however, is more spectacular for the ureolytic ones as the R:C and Rp:C ratios for this group are several times higher than that of the total as well as nitrate-reducing bacteria.

The above results indicate that the exudates from the roots of growing wheat crops can stimulate selectively the growth of the groups of bacteria responsible for the hydrolysis of urea and reduction of nitrates. This high population in root regions is likely to hasten up the process of urea transformation when applied to soils with growing crops and is likely to have a bearing on the nitrogen economy of soils.

Further studies are, however, essential with some more crops grown under different agro-climatic regions for generalisation of the above conclusion.

Acknowledgement

Thanks are due to Sri B. K. Dutta, Deputy Superintendent, Planning and Development Division, for evincing keen interest in the problem.

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[Original mss. received on 9.7.69]

Errata : Technology 6 (1969) Nos. 2 & 3

1. Paper: ESR and Optical Studies on Copper-Biuret Complexes
(i) On page 109, 6th line from bottom (1st column) please read normalized

$$\text{to } \int_0^a R^*_{n,1} R_{n,2} r^2 dr = 1$$

- (ii) On page 112, 5th line from bottom (2nd column) please read crystal field²⁴⁻²⁷.
2. On page 135 of the paper "On the Calculation of Multicomponent Extractive Distillation", please read the legends for the Fig. 1 as:
 - a Dimethyl formamide—Isobutyline temp. 20°C
 - b Dimethyl formamide—Methyl acetylene temp. 20°C
 - c Dimethyl formamide—Vinyl acetylene temp. 10°C

——Experimental
 Redlich Kister with vapour phase corrections

A simple instrument using an indigenous analytical balance has been described which can be used for simultaneous differential thermal and thermogravimetric analyses. Test results show that the instrument has a reasonably good accuracy. Its application to the study of catalysts has also been examined in order to establish its usefulness as a valuable quality control tool in catalyst development and manufacture.

A Combined DTA-TGA Unit—Its Design, Fabrication and Use in Catalyst Development

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In industrial catalysts development and manufacture there are certain heat treatment processes, by careful control of which it is possible to impart to finished catalysts, requisite properties like phase configuration, formation of solid solutions, mechanical strength, stability and their life in commercial reactors. Both DTA and TGA have been used separately in evaluating reactive solids during heat treatment operations, but a combined use of these techniques reveals a better picture of the solid under test. A number of authors¹⁻⁸ have reported methods of converting analytical balances to thermogravimetric balances separately or as simultaneous TGA-DTA units.

It was felt necessary to have a number of such combined units for research and quality control work in this laboratory. Since such units are costly, the design and fabrication of such an instrument from indigenously available components was therefore undertaken. This paper describes in details the necessary steps involved in the design, fabrication and calibration of the instrument, and its use in the studies on CO-conversion catalyst.

Design and Fabrication of the Instrument (Figs. 1 & 2)

A double pan, analytical balance (Fig. 1A) fitted with a mechanical ring rider weight-loading device was selected for this purpose. The action-arrest mechanism fitted at the base of the balance for the left pan was removed. This left a hole of *ca.* 1 cm. diam. on the base on left hand side under the pan. A hole of 3 mm. diam. was carefully drilled in the centre of the left pan. A 5 cm. long brass rod of 3 mm. diam. (Fig. 2A) threaded at

one end and was fixed through the hole of the pan and was suspended vertically downwards in centre position by means of a lock nut (L). It was connected to a hollow alumina rod (length 15 cm., diam. 4 mm.) by a metallic connector (Fig. 2B). The pan was placed on the beam and was held in its original position, with the brass and alumina rods passing through the hole in the base of the balance and hanging freely downward (Fig. 1B). Such a modified balance was mounted on a mild-steel stand so that the furnace (Fig. 1C) could be mounted immediately below the left pan.

While for DTA a small quantity of sample is heated at fairly high heating rates, TGA requires a comparatively large quantity of sample and lower heating rates. A special type of ceramic cell (Fig. 2C) having two

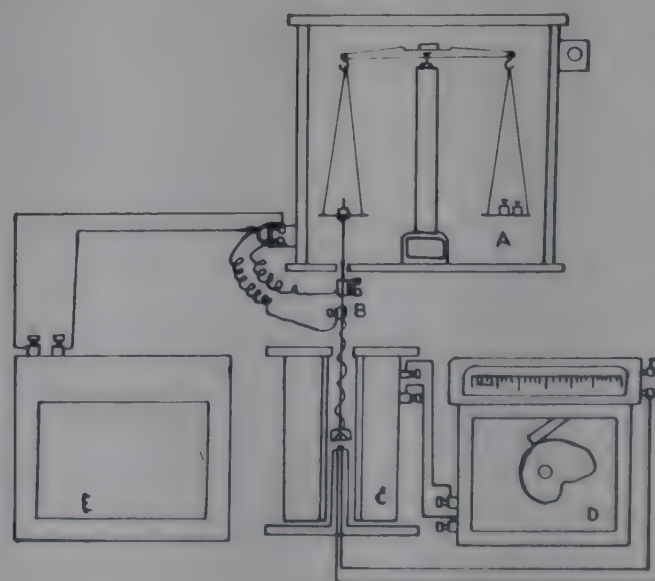


Fig. 1

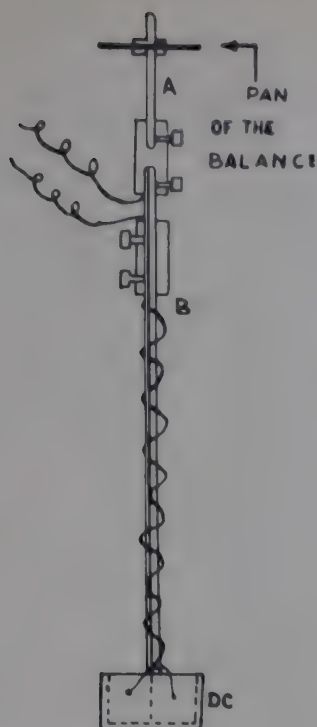


Fig. 2

cubical compartments was chosen as a compromise for the combined operation. The cell was held in position with the suspended alumina rod by a pair of a alumel-chromel thermocouples, which were also used for measuring the differential temperatures. Both the thermocouples were so arranged that their beads were placed centrally in the wells of the cell. The chromel leads were short-circuited in the cell itself, while the two alumel leads were taken out, one through the hollow alumina rod and the other lead held in position by a small connector; the inner lead was fastened with the connector coupling the brass rod and the alumina suspension. From these two connectors two separate thin-enamelled copper wires, *ca.* 48 s.w.g. and 20 cm. in length, were taken to small board fixed on the panel of the balance. Two leads from the board were then connected to the strip chart recorder (Fig. 1E) for DTA by means of a shielded two core cable.

Two 0.1 mfd. capacitors were connected between the leads and ground to avoid any stray electric pick up. The copper wire leads were arranged in large loops to minimize the drag on the balance. The furnace, with one end closed with an alumina block, was raised to position so that the alumina suspension assembly with cell was located centrally in the furnace. An alumel-chromel thermocouple was placed in the furnace in the close vicinity of the cell for the control and indication of furnace temperature, and the leads of this thermocouple were taken out through the two small holes in the alumina block sealing the lower end of the furnace and taken to a programme controller-cum-pyrometer (Fig. 1D). A heating rate of 7°C/min. was maintained.

The complete weight of the metallic rod, alumina rod and cell was counter-balanced by putting weights on the right hand pan, so that the pointer of the balance stood near the centre of the 0-100 mg. scale. In case of loss or gain of the sample, the reading from the scale could be taken directly. When the pointer crossed zero or 100 mg. mark on the scale showing either loss or gain of 100 mg., an additional 100 mg. weight was added or removed from the right hand side of the beam by means of mechanical weight loading arrangement originally provided with the balance. The mechanical weight loading dial was kept at such a position that a total weight-loss of the sample or an equivalent gain in weight could be observed easily by manipulating the dial in either direction.

CALIBRATION AND APPLICATION

Experimental

(1) For calibration and standardization of the instrument, DTA and TGA runs were made on calcium oxalate monohydrate and pentahydrate copper sulphate (Commercial A. R. grade). The former was prepared by adding a dilute solution of ammonium oxalate to a warm solution of calcium nitrate; the precipitate was washed filtered and dried at 110°C.

A weighed sample (*ca.* 0.5-0.8 g.) was transferred into one compartment of the sample-holder (Fig. 2) and about 0.5 g of inert material (alumina ignited at 1000°C) was placed in the other. The weight of the sample-holder assembly was counter-balanced as described earlier. The output from the differential thermocouples was taken to the recorder. The readings for the change in weight were taken as a function of temperature indicated by a pyrometer. Simultaneous DTA-TGA curves obtained with our instrument for the standard substances are given in Figs. 3 and 4. Calcium oxalate decomposition data are given in Table 1.

TABLE 1

Peak Temp., °C	Composition	Component Loss	Theoretical Loss, %	Experimental Loss, %
200	CaC ₂ O ₄ ·H ₂ O	Water of hydration	12.32	12.21
400	CaC ₂ O ₄	CO	19.18	18.98
	CaCO ₃	—	—	—

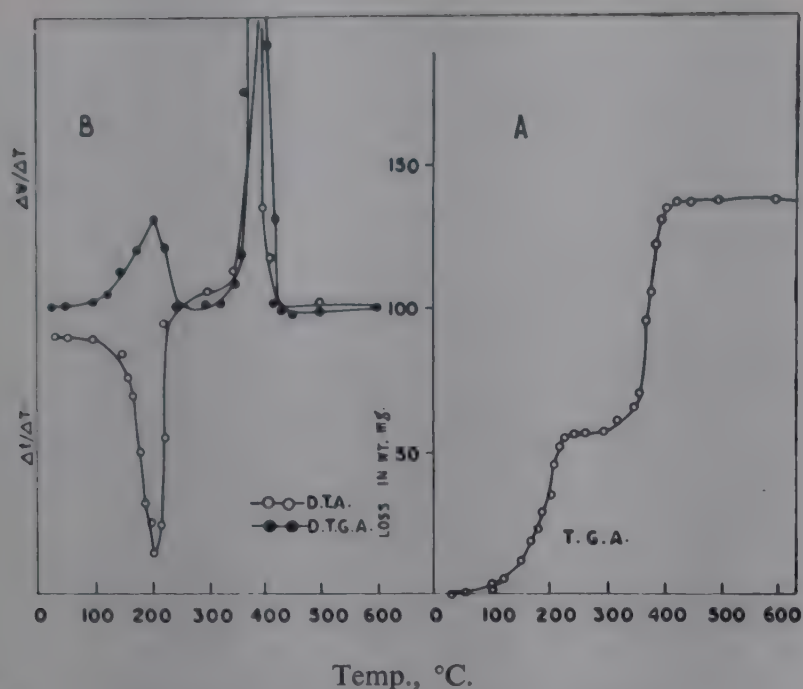


Fig. 3—D.T.A., T.G.A. & D.T.G.A. Curves of Calcium Oxalate obtained from the Modified Balance (Heating Rate 7°C/mm; Sample Weight 0.4 g.)

(2) For examining the suitability of the instrument in the development and commercial production of catalysts, it was used for DTA-TGA studies on a CO-conversion catalyst. The following samples were taken from three different stages of its production: (i) iron oxide dried at 120°C; (ii) iron oxide cured at 350°C for 5 hr. and (iii) the same cured at 450°C for 5 hr. Simultaneous DTA and TGA runs were made on the above three samples (Fig. 5).

Results and Discussion

Thermal decomposition of calcium oxalate is a very well-known reaction. Duval³ and others have used this compound as a standard for the calibration of thermogravimetric balances. From its DTA-TGA and DTGA curves (Fig. 3), it can be seen that well matches peaks appear for both DTA and DTGA, at about the same temperatures. The first peak at 200°C in case of DTGA indicates the loss of one water molecule and a peak at the same temperature (endothermic) in case of DTA represents the same phenomenon. The second peak at 400°C on DTGA and DTA shows that decomposition of dehydrated calcium oxalate has taken place between 380 and 390°C with the evolution of carbon monoxide. The quantitative matching of experimental and theoretical weight-losses at these two stages (Table 1) confirms the accuracy of the balance within experimental limits. These curves have been discussed in detail by De Keyser⁹.

Again, decomposition of copper sulphate (Fig. 4) shows the loss of water molecules in two stages. Four molecules of water are lost between 100 and 200°C

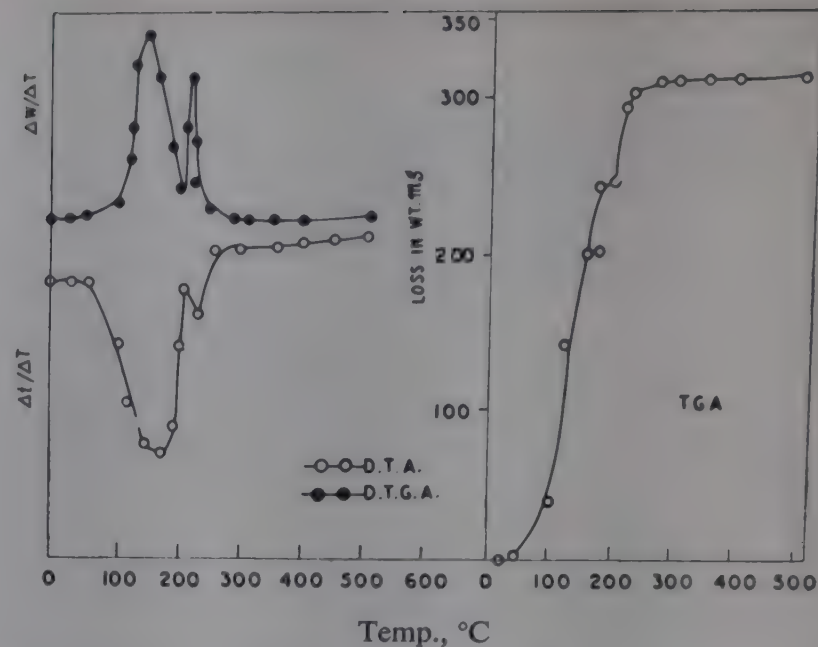


Fig. 4—D.T.A., T.G.A. & D.T.G.A. Curves for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

and the last molecule is liberated between 200 and 300°C, which corroborates with the published data.¹⁰

DTA and DTGA curves for the iron oxides are shown in Fig. 5. Sample (1) shows two distinct endothermic peaks in DTA and DTGA at 150 and 350°C. respectively, the former being due to the liberation of adsorbed moisture, while the latter indicates the loss of combined water with the associated phase transformation according to the following equation:

$2 \text{FeO}(\text{OH}) \text{ (rhombic)} \rightarrow \text{Fe}_2\text{O}_3 \text{ [cubic]} + \text{H}_2\text{O}$. This transformation has been discussed in detail by Mackay¹¹.

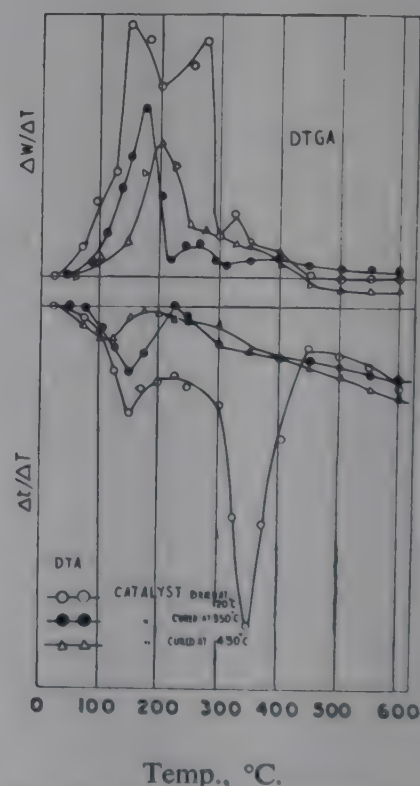


Fig. 5—D.T.A. & D.T.G.A. Curves of CO-Conversion Catalyst

It can be observed from this set of curves that the second peaks become less prominent in the case of samples cured at higher temperatures, although a complete transformation is not seen even in the case of the third sample. These curves provide valuable information regarding the progress of the curing process. It is also seen that the capacity of the samples to hold adsorbed moisture decreases with increasing curing temperature, due to changes in structure porosity. The reported exothermic change of Fe_2O_3 (cubic) to Fe_2O_3 (hexagonal) is not marked in these samples, which may be due to the method of preparation of the original oxide mass.

In accordance with the above results and discussions, it can be said that our instrument fabricated out of indigenous components has a reasonably good accuracy. Thus, it can be used to provide valuable guidance in the development and quality control of catalyst manufacture.

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Calcium, strontium and barium have been studied in air-hydrogen and air-acetylene flames. In the case of hydrogen, the usual acetylene burner-head and the wider slot burner have been used. The sensitivity of the these elements is slightly higher in air-hydrogen flame using acetylene burner and significantly improves in the wider slot burner. The interferences are more in the air-hydrogen flame than in the air-acetylene flame. Lanthanum chloride releases the phosphorus and aluminium interferences in both the flames. The effect of EDTA on calcium has been investigated.

Atomic Absorption Study of Alkaline-Earth Elements in Air-Hydrogen and Air-Acetylene Flames

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The estimation of alkaline-earth elements by atomic absorption is of special interest because the analyses suffer interference from a host of ions whose occurrence in the analyses of these elements is quite common. The estimation appears to be simple but requires a careful

attention and proper release or protection of these analyte atoms from the interfering ions. A lot of investigations¹⁻⁹ have been done for these elements in different flames. The interferences are supposed to be due to the formation of involatile compounds of the analyte with

the interfering ions in the flame, which do not dissociate completely in the flame. Nitrous oxide-acetylene flame is being preferred to the high temperature oxy-hydrogen flame due to its reasonably high temperature (2950°C) and lower burning velocity. Ramakrishna et al⁵ have used the oxy-hydrogen flame for estimation of calcium and found that in spite of high temperature (3000°C) the analysis was not still free from interferences. The same workers⁷ have used air-acetylene and nitrous oxide-acetylene flames for calcium.

The potentialities of air-hydrogen flame have not been studied so far in detail. Only Slavin et al³ have studied the above elements in this flame and observed that the interferences are more due to its low temperature and the sensitivity is comparable to that of air-acetylene. Air-hydrogen^{10,11} and argon-hydrogen entrained air flames¹² are now being used profitably for the estimation of arsenic, cadmium, etc., because at wave length near 2000 Å flame absorption in the above flame is much less than in the conventional flames.

The present work is a part of the investigation in connection with the estimation of phosphorus by its depressing effect on strontium and calcium. The depression is more on strontium¹³ than on calcium¹⁴ in an air-acetylene flame. To achieve better accuracy, it was thought necessary to investigate the air-hydrogen flame for the estimation of phosphorus because the interference due to phosphate was expected to be more in air-hydrogen than in the air-acetylene flame.

Experimental

Reagents Used: (1) 1000 ppm of strontium soln. prepared from strontium carbonate with a minimum amount of hydrochloric acid; (2) 1 per cent calcium solution (Herleco, Philadelphia); (3) 1000 ppm barium prepared from barium chloride; (4) 1 per cent sodium solution (Herleco, Philadelphia); (5) 1000 ppm phosphorus prepared from di-sodium phosphate after passing through Amberlite IR-120 (H⁺); (6) 1000 ppm of aluminium prepared by dissolving pure aluminium in hydrochloric acid (conc.); (7) 5 per cent lanthanum solution having 25 per cent hydrochloric acid by dissolving

lanthanum oxide in hydrochloric acid (conc.) and (8) 5 per cent solution of di-sodium salt of ethylene-diamine tetra-acetic acid (EDTA).

Instrument: A Perkin-Elmer 303 atomic absorption spectrophotometer, equipped with a standard air-acetylene burner head (10 mm × 0.5 mm), with an automatic recorder and P-E hollow cathode lamps, was used. The slot of nitrous oxide-acetylene burner (part No. 303-0195) was modified to 75 mm × 1 mm. for use for air-hydrogen flame.

Procedure: The procedure as recommended in the standard analytical methods¹⁵ was followed. The flow of air-acetylene and hydrogen and the burner height were adjusted for the particular element to achieve the maximum absorption. The modified nitrous oxide burner was used to determine the sensitivity in the air-hydrogen flame, which sometimes gives a little pop while putting it off. The other conditions are given in Table 1.

Results and Discussion

It was observed that the sensitivity of calcium and strontium was slightly higher for air-hydrogen flame (Fig. 1) than the air-acetylene flame, when the same

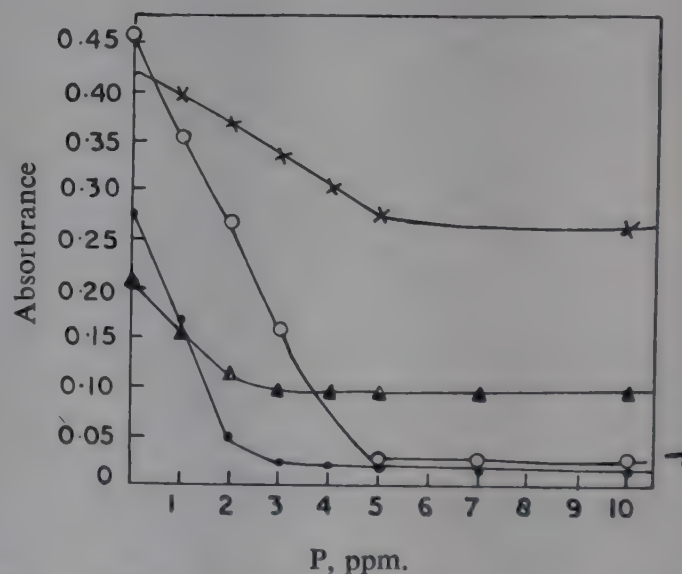
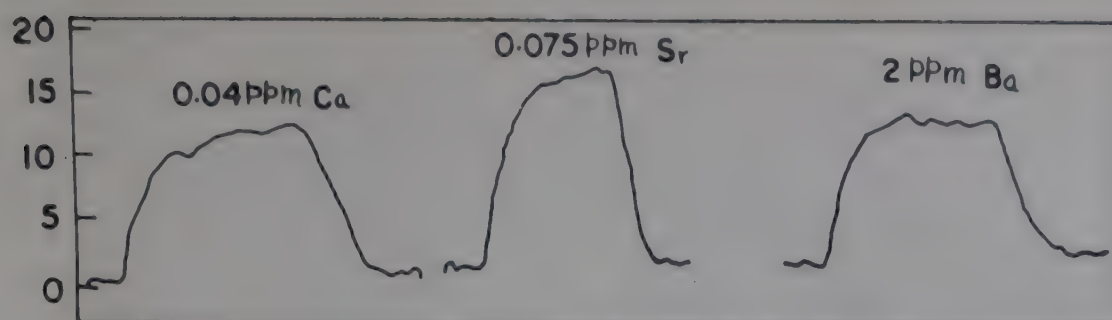


Fig. 1—Effect of Phosphorus on Strontium and Calcium
Air/C₂H₂ Air/H₂
▲ — Sr 10 ppm; ● — Sr 10 ppm
× — Ca 10 ppm; ○ — Ca 10 ppm

TABLE 1—ANALYTICAL CONDITIONS

Element	Atomic Line, Å	Current, ma.	Slit, mm.	Meter Response	Pressure, psi.		
					Air	Acetylene	Hydrogen
Ca	4227	10	1	2	30	8	15
Sr	4607	10	1	2	30	8	15
Ba	5536	20	0.3	2	30	8	15



Scale x10 and Noise Suppression-4

Fig. 2—Recorder Tracing of Calcium, Strontium and Barium

standard acetylene burner was used for both the fuels. When modified nitrous oxide burner was used for air-hydrogen flame the sensitivity of calcium and strontium improved significantly while the barium sensitivity improved in air-hydrogen flame but same in both the burners. The recordings are given in Fig. 2. The sensitivities of calcium, strontium and barium obtained from air-hydrogen flame in modified nitrous oxide burner are compared (Table 2) with the air-acetylene flame in a standard burner¹⁶ and with the sensitivity obtained by Amos in nitrous oxide-acetylene flame using the Techtron instrument¹⁷. Since in air-hydrogen flame the noise is less, detectability would also improve accordingly.

TABLE 2—SENSITIVITY IN DIFFERENT FLAMES

Element	Sensitivity $\mu\text{g/ml}/1\%$ absorption		
	Air-acetylene ¹⁶	Air-hydrogen*	Nitrous oxide-acetylene ¹⁷
Ca	0.1	0.04	0.03
Sr	0.2	0.05	0.06
Ba	5.0	2.00	0.40

*wide slot burner

It was obvious from Intonti's⁹ observations that the sensitivity of strontium in air-propane flame (1900°C) was very much less than in the air-acetylene flame (2300°C). The temperature of air-hydrogen flame (2000°C) lies between those of the air-acetylene and air-propane flames, but the sensitivity in air-hydrogen flame was not so. This shows that though the ground state atoms in low temperature flame are more, the other chemical nature of flame is playing part. Probably the formation of alkaline-earth oxide in the air-hydrogen flame is less than the air-acetylene flame. The increase in sensitivity in a modified nitrous oxide burner was due to the broader flame, thereby more atoms come in the path of light beam. Amos¹¹ has used the burner almost of the same design for air-hydrogen flame of slot dimension 100 mm $\times$ 1 mm. The sensitivity in longer

slot as that of Amos may increase further which is inherently safe also. The sensitivity of these elements did not increase further in argon-hydrogen entrained air flame due to its low temperature. But in case of fluorescence, Veillion et al¹⁸ have already observed 10-fold increase in intensity for magnesium in the above flame. Zacha and Winefordner¹⁹ have also observed the improvement of emission intensity for some elements in argon-hydrogen entrained air flame over oxy-hydrogen flame.

Interferences: The effect of phosphorus was studied on calcium and strontium in both the air-acetylene and air-hydrogen flames (Fig. 1). The interference in the latter flame is much more than in the former. The sharp bend in the curves correspond to 3:2 mole ratio of Ca or Sr: P; thereafter further addition of phosphorus has no effect and curves run flat. The effect of aluminium on strontium was also studied in both flames (Fig. 3) and it was observed that the absorption gradually decreases with the increase of aluminium.

It was observed that the strontium was completely recovered from 100 ppm phosphorus in air-hydrogen flame and from 200 ppm phosphorus in air-acetylene flame by 1 per cent lanthanum. Though lanthanum

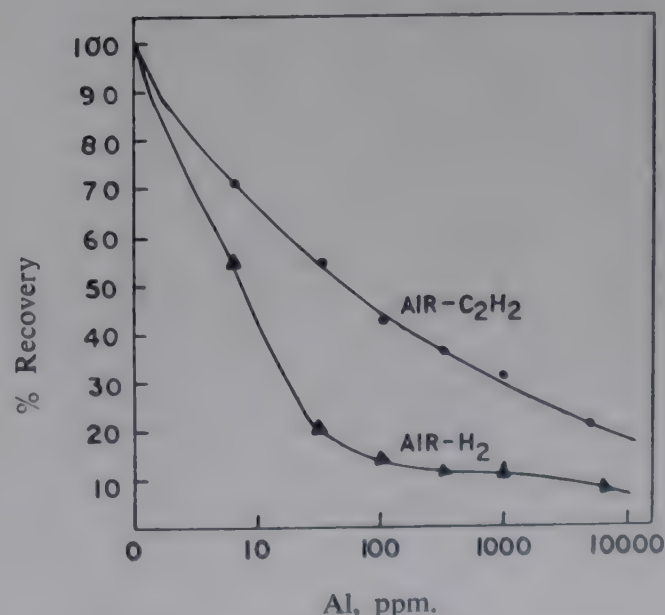


Fig. 3—Effect of Aluminium on Strontium

overall decreases the strontium absorption in air-hydrogen flame, 1 per cent lanthanum recovered the total strontium from 200 ppm of aluminium in air-hydrogen flame, but in air-acetylene flame slightly more aluminium is tolerated. It was also observed that strontium chloride releases calcium from phosphorus, without decreasing the overall absorption.

Effect of EDTA: West and Cooke²⁰ have used an ammonium salt of EDTA to eliminate the interference of phosphorus on calcium in flame emission. The mechanism of the releasing agent, like lanthanum, is well-known but the nature of the organic compounds and the chelating agent is not very clear. The protection of the analyte atoms from the interfering ion is not necessarily due to chelate formation as some of organic compounds, like utropine, glucose, etc, which do not make chelate, release the interferences. The EDTA (its di-sodium salt) study was made at different pH and it was observed that the EDTA protects the calcium from 5 ppm phosphorus at almost all pH, in air-acetylene flame while the chelate formation is only in alkaline pH. The recovery of calcium at different concentrations of EDTA for phosphorus (Fig. 4) and aluminium (Fig. 5) was made at different burner heights. In air-acetylene flame about 0.5 per cent EDTA recovers calcium from 5ppm EDTA but in air-hydrogen it does not recover at all. EDTA addition in presence of aluminium first decreases the calcium absorption at low concentration and then with increasing amounts of EDTA recovers the calcium from aluminium in an air-acetylene flame.

In air-hydrogen flame addition of EDTA in presence of aluminium suppresses the absorption even further.

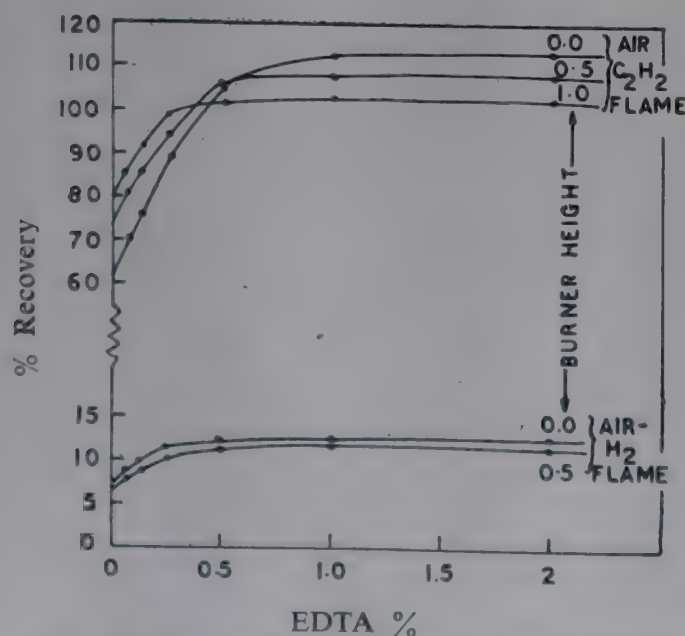


Fig. 4—Effect of EDTA on Calcium in Presence of 5 ppm of Phosphorus at Different Burner Heights

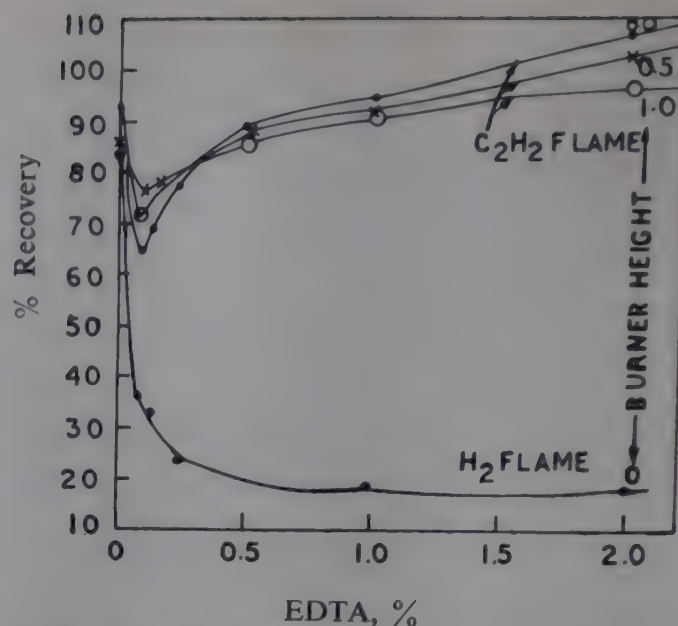


Fig. 5—Effect of EDTA on Calcium in Presence of 5 ppm of Aluminium at Different Burner Heights

The effect of varying amount of EDTA on calcium is shown in both the flames (Fig. 6). EDTA alone also suppresses the calcium absorption in air-hydrogen flame. The behaviour of EDTA in air-hydrogen flame as well as the difference in the behaviour in air-acetylene and air-hydrogen flames would not be explained by the physical properties like surface tension, viscosity, evaporation rate and aerosol drop size^{21,22}. This decrease in air-hydrogen flame may be due to its lower temperature.

Conclusion

Alkaline-earth elements are more sensitive in air-hydrogen flame than in the air-acetylene flame. In the broader slot burner the sensitivity significantly increases. Due to the lower temperature the interferences are also more in air-hydrogen than the air-acetylene flame. The former can be used for the estimation of these elements. The increased interferences can be compensated with

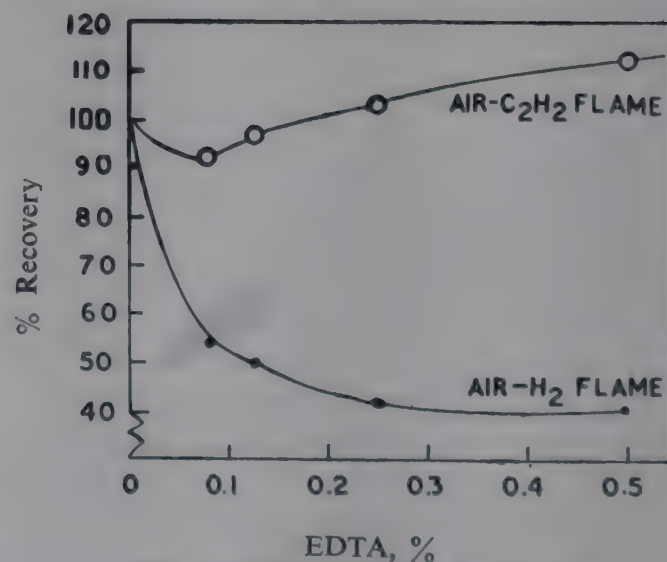


Fig. 6—Effect of EDTA on Calcium

the increase in sensitivity by working in less interfering and less sensitive zone of the flame. Lanthanum can be used to release the atoms from the interfering ion in air-hydrogen flame as in air-acetylene flame. Similarly strontium chloride can be used for releasing the calcium for interfering ions in both the flame. EDTA cannot be used to protect these atoms from interfering ions in air-hydrogen flame, unlike air-acetylene flame. Air-hydrogen will prove superior to air-acetylene flame for indirect estimation of phosphorus employing its depressive effect.

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Ammonium bicarbonate samples have been concentrated by decomposition in boiling water, and chloride has been estimated by determining the excess silver using silver nitrate method and the excess barium for sulphate determination by the barium sulphate method. The precision of both the estimations was about 5 per cent for concentration levels present.

Estimation of Chloride and Sulphate in Ammonium Bicarbonate by Atomic Absorption Spectrophotometry

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Ammonium bicarbonate (ABC), a fertilizer-allied product, is an important material for food industry. The determination of metallic and non-metallic impurities in it, is required for its quality control and standardization¹. In our earlier work² some metallic impurities have been estimated by atomic absorption spectrophotometry (AAS). The present work has been undertaken with a view to estimate the non-metallic impurities, e.g. chloride and sulphate in the ABC samples using the above technique.

The estimation of chloride and sulphur poses problems for estimation by flame spectroscopic technique, since the principal resonance lines of these non-metallic elements fall in vacuum ultraviolet which is outside the range of the common spectrophotometers. The direct method for estimation of chloride and sulphur is based on the emission intensity measurement of molecular bands. Honma³ has modified the Beilstein identification test for chloride for its quantitative estimation. The CuCl band peak of the D system, which occurs at 435.4 m μ , has been used for chloride estimation by him. Marsh⁴ has also used the same band for estimation of organic chloride. Recently, Dagnall et al⁵ have estimated sulphur with the emission measurement of S₂ band at 384 m μ using hydrogen-nitrogen diffusion and shielded air-hydrogen cool flames. These low temperature flames are most suitable for the production of S₂ bands. Syty and Dean⁶ also estimated sulphur in the shielded fuel-rich air-hydrogen flame, by using the violet S₂ bands. These direct methods cannot be used

for atomic absorption technique, which is specifically based on absorption by atoms.

The indirect method for these anions are based on the addition of excess of metal salts to the sample solution which undergoes precipitation reaction with the element to be determined either in the form of simple or complex anion. Chloride and sulphate are precipitated as silver chloride and barium sulphate respectively. The precipitate is dissolved in a suitable medium^{7,8}, and the cations are estimated by AAS which gives the corresponding anion concentration.

In the present determination, the ABC samples were decomposed as earlier², in boiling water and chloride was estimated by precipitating it as silver chloride and estimating excess silver in the filtrate⁹. In the case of sulphate, the excess barium was estimated similarly. The "excess method" was adopted as it saves one step of dissolving the precipitate in a suitable solvent. Moreover, the chloride and sulphate contents in ABC samples being low, the amounts of silver and barium in the working solutions do not fall in the optimum analytical range. In the case of sulphate, though its content was not very low but in the available air-acetylene flame, the sensitivity of barium is poor and therefore "excess method" has been used.

Experimental

(A) Sample Preparation

(i) *Chloride Estimation*: 40 g. of ten different ABC samples were decomposed in about 20 ml. of boiling

water in 50 ml. conical flasks. 5 ml. of 20 per cent nitric acid was added to each solution and boiled for 2 min. Then 5 ml. of 200 ppm silver solution (prepared from silver nitrate) was added to the boiling solutions and then cooled for about 45 min. in dark. After filtering, the volume was made to 50 ml. by washing with 1 per cent nitric acid. The filtrates were used for the estimation of excess silver.

(ii) *Sulphate Estimation*: 40 g. each of Nos. 1 to 5 and 20 g. of Nos. 6 to 10 of ABC samples were decomposed, as earlier², in boiling water till the volumes were reduced to about 20 ml. In case of samples from No. 6 to 10, the quantity of ABC was taken less as these were found to contain more sulphate. To each of the above samples, 2 ml. of 10 per cent hydrochloric acid was added. After heating on a hot plate, 5 ml. of 10 per cent barium chloride dihydrate solution was added to each. After cooling, the volumes were made to 50 ml. and filtered. The filtrates were used for estimation of excess barium.

(iii) *Recovery Test*: For testing the reliability of the present method for ABC samples, recovery tests were carried out. For chloride, 20 g. each of ABC No. 7 was taken in five flasks and 0, 2, 4, 6 & 8 ml. of a 25 ppm chloride solution (as $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) were added in them respectively and the working samples were prepared for chloride estimation as earlier.

For sulphate, 20 g. each of ABC sample No 11 was taken in four conical flasks and 0, 5, 7.5 and 10 ml. of a 1000 ppm sulphate solution (as sodium sulphate) were added respectively. The working samples were prepared as earlier.

(iv) *Reproducibility Test*: For finding out the reproducibility, two ABC samples were decomposed in bulk and ten aliquots were taken separately for chloride and sulphate estimations.

(B) Standards

5, 10, 15 & 20 ppm silver standards were made from silver nitrate. Each standard solution contained 2 per cent nitric acid. For sulphate estimation, barium standards of 112.4, 280.9 and 561.8 ppm containing 0.4 per cent hydrochloric acid were prepared. The acid concentrations in all the standards were kept nearly same as in the working samples.

For all the samples and standard preparations, G.R. or A.R. quality reagents and de-ionized water were used.

(C) Procedure

Perkin-Elmer model 303 atomic absorption spectrophotometer and silver and barium hollow cathode lamps

of the same make were used. The analytical conditions were followed as suggested in analytical methods¹⁰, except that, in case of barium estimation air-acetylene flame was used due to non-availability of nitrous oxide-acetylene flame.

Firstly, the zero of the instrument was adjusted by aspirating de-ionized water blank and then the standards, the working samples and the solutions for recovery and reproducibility tests were aspirated in the flame and corresponding absorptions were found out. Calibration curves of silver and barium are given in Figs. 1 & 2 respectively. The amounts of silver and barium consumed for precipitation of chloride and sulphate respectively were found out by determining the excess of silver and barium in the solutions and subtracting them from their amounts added originally. Equivalent chloride and sulphate contents in the samples were calculated.

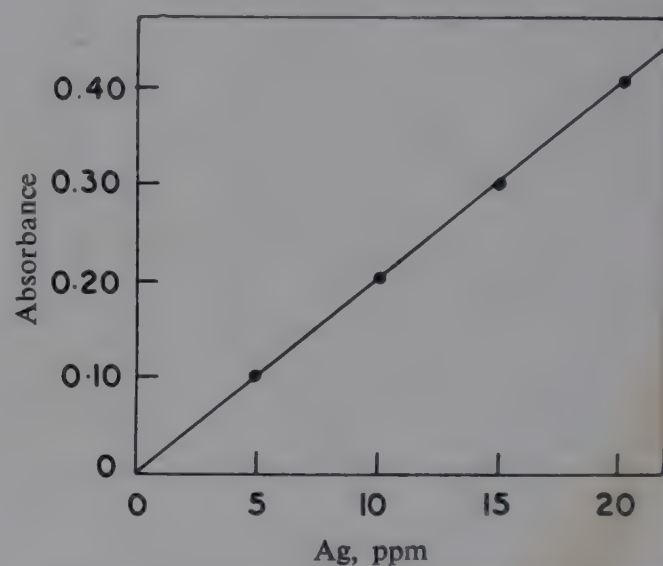


Fig. 1—Calibration Curve for Silver in Chloride Estimation

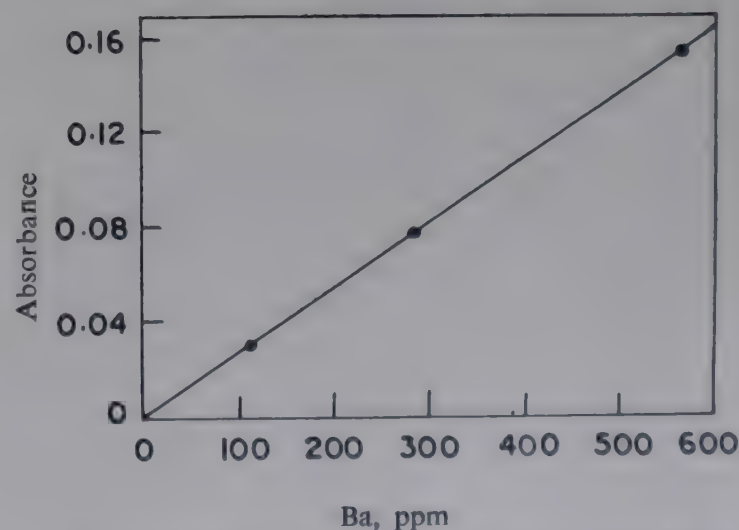


Fig. 2—Calibration Curve for Barium in Sulphate Estimation

TABLE 1—CHLORIDE AND SULPHATE IN AMMONIUM BICARBONATE SAMPLES, PPM.

Sample No.	Chloride	Sulphate
1	2.71	139.8
2	2.84	43.6
3	1.31	51.5
4	1.97	86.0
5	1.81	94.7
6	2.10	304.5
7	3.74	604.2
8	1.41	235.8
9	3.52	221.2
10	3.29	296.6

Results and Discussion

The results of analysis of chloride and sulphate in ten ABC samples are given in Table 1. The decomposition method used in the present work has been found quite satisfactory as the recovery of the chloride as well as sulphate added to the sample before decomposition was quite good. This is evident from the recovery data

(Table 2) which shows a recovery of 95.2 to 100.5 per cent for chloride and 95.8 to 98.8 per cent for sulphate additions. The reproducibility of precipitation and estimation of excess metals in decomposed ABC samples was obtained as 1.0 per cent for chloride and 2.1 per cent for sulphate.

The chloride as well as sulphate contents in the samples are well within the maximum allowable limits (chloride 0.5 per cent and sulphate 0.1 per cent) as specified by the Indian standards¹ for use of ABC in food industry. In the case of sulphate, even lower concentration can be estimated in the nitrous oxide-acetylene flame since the sensitivity of barium is high in this flame and the interference of other ions, like phosphate, etc., is absent. In air-acetylene flame, the interference on barium is expected from ions like phosphate etc. but in the present study, ABC samples are found to be free from them. Estimation of chloride and sulphate with excess method using atomic absorption spectrophotometry can also be adopted for other materials. Care has to be taken for interfering ions (if present) in case of sulphate estimation by using a suitable releasing agent.

TABLE 2—RECOVERY FOR CHLORIDE AND SULPHATE

Chloride Recovery					Sulphate Recovery				
Sample No.	Added, ppm.	Estimated, ppm	Recovered ppm	% Recovery	Sample No.	Added, ppm	Estimated, ppm	Recovered, ppm	% Recovery
7	0.00	3.78	0.00	—	11	0.00	335.9	0.00	—
7—A	2.50	6.16	2.38	95.2	11—A	250	581.5	245.6	98.2
7—B	5.00	8.71	4.93	98.6	11—B	375	695.3	359.4	95.8
7—C	7.50	11.32	7.54	100.5	11—C	500	830.1	494.2	98.8
7—D	10.00	13.72	9.94	99.4					

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The simple circuit described here is used for fixed point liquid level indication and control, which is best suited for indoor working. It is useful for metallic contact (on/off) and all electrolytes up to the conductivity of tap water within an ambient temperature range of 10 to 40°C

Design of an Electrode-Type Transistorized Level Switch (On-Off Controller) and Its Applications—I

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Liquid level switches are used mainly in plants for the indication and control of liquid levels. These may also be utilized in research laboratories and other organisations where the switching action is desirable to be actuated by means of a liquid level or a metallic contact.

There are commercially available level switches operating electronically. In this paper, a simple transistorized circuit has been described; it has been designed from easily available components and found to be working satisfactorily.

Transistor Circuit

The design of the circuit is based on a supposedly inherent drawback of a transistor, viz. the leakage current, which however acts as a useful property for this switching action.

It is known that a transistor gives rise to a leakage current when a potential difference of opposite polarity is applied across any two of its terminals. The collector-base leakage current (flow of electrons) flows from the collector to the base (with the emitter terminal open) for a PNP transistor and is represented by I_{CBO} (Fig. 1). Similarly, a collector-emitter leakage current flows from the collector to the emitter (with the base open) when the former is made negative with reference to its emitter and is represented by I_{CEO} . These two currents are related by the following $I_{CEO} \approx \beta I_{CBO}$ (1), where β is the current gain of the transistor in the common emitter configuration. It is obvious from equation (1) that the existence of I_{CEO} is due to the presence of I_{CBO} . It is better understood as follows:

As I_{CBO} flows from the collector to the base and the base terminal is open, it crosses the base-emitter junction and due to the transistor action its value increases β times and thus I_{CEO} flows from collector to emitter and it is a measurable quantity.

It is also clear from equation (1) that if by some means the value of I_{CBO} is decreased then I_{CEO} will also decrease proportionately to β times of the decreased value of I_{CBO} . This is achieved by putting a resistance R_B between base and emitter terminals (Fig. 2). Now, a fraction of I_{CBO} , which is represented as I_{CB} , flows through R_B and the remaining part ($I_{CBO} - I_{CB}$) crosses the base emitter junction and gives rise to $I_{CE} = \beta(I_{CBO} - I_{CB})$. If $R_B = 0$, almost full value of I_{CBO} —depending upon the values of r_b and r_e —flows through R_B and practically I_{CE} becomes zero. Thus, it is concluded that the value of I_{CE} can be varied from 0 to I_{CEO} only by changing the value of R_B from 0 to the open circuit value. This is the fundamental basis of control of the transistor switch circuit.

The leakage current, I_{CE} , of a low level transistor so obtained is fed to the base of a medium power transistor, which is amplified β times in its collector-emitter circuit.

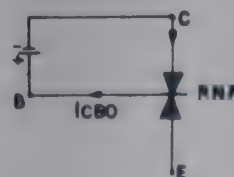


Fig. 1

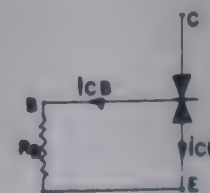


Fig. 2

If a relay load is placed in the collector or emitter circuit of the output transistor, it gets energized if the points A and B are kept open and de-energized when shorted through a column of resistance within the controlling range. Such a practical circuit is shown in Fig. 3, where T_1 is the controlling transistor with the control points A and B and T_2 is the output transistor which delivers the power to a relay coil.

Design

The circuit is designed using the transistors $T_1=AC\ 125$; $T_2=AC\ 126$ and a relay coil of resistance 200 ohms. The operating data of the transistors, measured by means of a transistor tester at $25^\circ C$, are given as follows:

For AC 125: (1) At $V_{CB}=5V$, $I_{CBO}=6\mu a$; at $V_{CE}=5V$, $I_{CEO}=600\mu a$.

(2) At $V_{CE}=5V$ and $I_C=0.5\text{ m.a.}$
 $h_{ie}=11.2K$, $h_{fe}\simeq 100 (= \beta_1)$

For AC 126 (1) At $V_{CB}=5V$, $I_{CBO}=8\mu a$; at $V_{CE}=5V$, $I_{CEO}=1.2\text{ m.a.}$

(2) At $V_{CE}=5V$, and $I_C=5\text{ m.a.}$
 $h_{ie}=1.8\text{ K}$, $h_{fe}\simeq 200 (\beta_2)$

It is found in practice that the minimum current required to actuate the relay is about 20 m.a. i.e. the voltage drop across the relay coil is $20\text{ m.a.} \times 200\text{ ohms} = 4\text{ volts}$. Therefore, a supply source of 6 volts can be used safely to operate the transistor circuit. The base current required for T_2 to have an emitter current of 20 m.a. is given by

$$I_{B_2} = \frac{I_{E_2}}{\beta_2} = \frac{20\text{ m.a.}}{200} = 100\mu a. \text{ And from the}$$

circuit, $I_{CE_1} = I_{B_2}$, the transistor AC-125 having $I_{CEO} = 600\mu a$, can be safely used as a control transistor. The higher current in the emitter circuit of T_2 will be limited by the supply conditions.

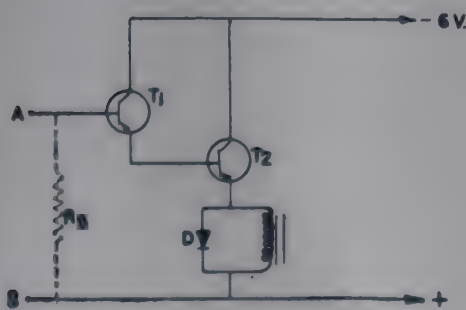


Fig. 3

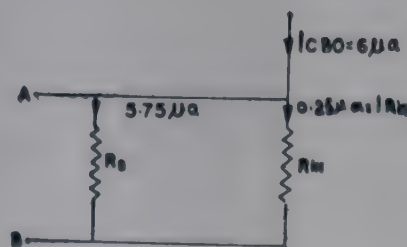


Fig. 4



Fig. 5

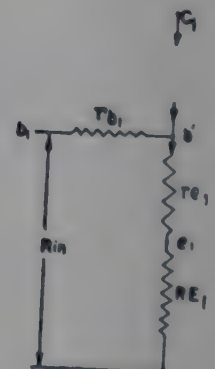


Fig. 6

It is desirable to calculate approximately the maximum value of R_B which can trip off the relay. It is also practically found that once the relay is pulled on, it goes off only when current just falls to about 5 m.a. From this it is clear that the switching action of T_2 takes place at 5 m.a. of its emitter current value. At that instant the collector-emitter current of T_1 is given

$$\text{by } I_{CE_1} = I_{B_2} = \frac{5\text{ m.a.}}{200} = 25\mu a. \text{ And the fraction of}$$

I_{CBO} which crosses the base-emitter junction of T_1 is obtained as $\frac{25\mu a}{100} = 0.25\mu a$. It means for a maximum

controlling value of R_B the fraction of I_{CBO} which crosses the base-emitter junction is only $0.25\mu a$, and it flows through the resistance R_{in} , the input resistance of the circuit (Fig. 4) and the remaining value of I_{CBO} ($=5.75\mu a$) passes through R_B . Hence to obtain this maximum value of R_B , it has become necessary to calculate the value of R_{in} at the switching current value.

For determining the value of R_{in} the following procedure may be followed: The low frequency T equivalent circuit of a transistor is shown in Fig. 5 where r_b , r_e and r_c are the intrinsic transistor parameters of the corresponding terminals w.r.t. a common point b' in the active region of the base. For all practical purposes r_c may be considered as open-circuit and neglecting the internal feed-back the input resistance in common collector circuit is given by $R_{in} \simeq r_b + \beta r_e$.

If this formula is applied to transistor T_1 having an emitter load of value R_{E_1} (as shown in Fig. 6) the input resistance $R_{in} \simeq r_{b1} + \beta_1 (r_{e1} + R_{E_1})$. (2)

From Fig. 3 the emitter of T_1 is connected to the base of T_2 so that the complete equivalent circuit of Fig. 3 is shown in Fig. 7, where $R_{E_1} = r_{b2} + \beta_2 (r_{e2} + R_{E_2})$ and the total input resistance of the circuit is given by $R_{in} = r_{b1} + \beta_1 [r_{e1} + r_{b2} + \beta_2 (r_{e2} + R_{E_2})]$

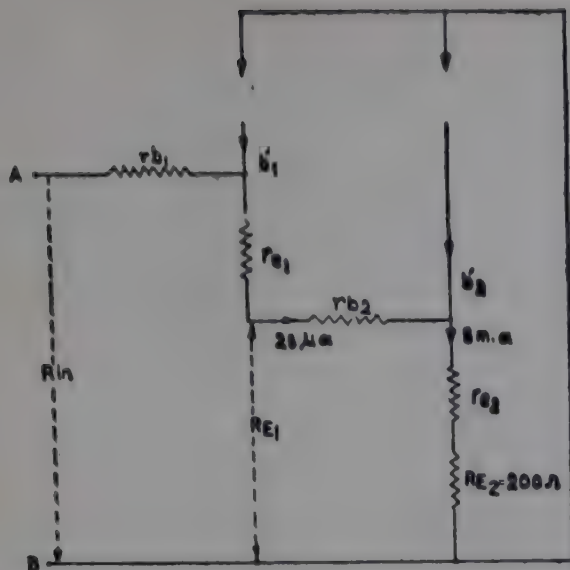


Fig. 7

But for leakage consideration point of view r_{b1} will come in the R_b path instead of R_{in} path, therefore $R_{in} = \beta_1 [r_{e1} + r_{b2} + \beta_2 (r_{e2} + R_{E2})] \dots \dots \dots (3)$

The emitter resistance, r_e is given by the relation

$$r_e = \frac{25}{I_e \text{ (m.a.)}} \text{ Ohms at } 25^\circ\text{C, where } I_e \text{ is the emitter current.}$$

Therefore for T_1

$$r_{e1} = \frac{25}{25 \times 10^{-3}} \text{ Ohms} = 1\text{K Ohms and from}$$

equation (3)

$$R_{in} = 100 (1\text{K} + 1.8 \text{ K} + 200 \times 0.2 \text{ K})$$

$$\text{where } r_{b2} + \beta_2 \cdot r_{e2} = h_{ie2} = 1.8\text{K.}$$

$$\text{and } R_{E2} = 200 \text{ Ohms, the coil resistance}$$

$$R_{in} = 4280 \text{ K.}$$

If $I_{R_{in}}$ is the current passing through R_{in} , as shown

$$\text{in Fig. 4 then, } \frac{I_{R_{in}}}{I_{CBO}} = \frac{R_B}{R_B + R_{in}} \dots \dots \dots (4)$$

or

$$\frac{0.25}{6} = \frac{R_B}{R_B + 4280 \text{ K.}}$$

$$\therefore R_B = 182 \text{ K.}$$

It means the relay circuit will be tripped off for any value of R_B between 0 and 182 K. The author has also found in practice that the relay circuit goes off for a value of R_B between 0 to 160 K, which is a good approximation towards the calculated value, though the value of r_{e1} has not been considered, which is quite comparable to R_{in} and lowers the effective value of R_B . This value of R_B will be different for different transistors of the same type as because I_{CBO} and β both

varies from transistor to transistor. The variation of R_B is very much sensitive towards the ambient temperature and it will be discussed later on.

The circuit under discussion can be used for low as well as high conductivity solutions. But its use in the high conductivity liquids may be limited if the liquid is forming foams, which may result in wrong indication of the liquid level. This drawback may be removed by a simple alteration in the circuit of Fig. 3. In the modified circuit (Fig. 8), the coil load is placed in the collector circuit rather than in the emitter circuit.

The input resistance of this circuit is obtained from equation (3) in which $R_{E2} = 0$.

$$R_{in} \approx \beta_1 (r_{e1} + r_{b2} + \beta_2 \times r_{e2}) = 100 (1\text{K} + 1.8 \text{ K}) = 280 \text{ K.}$$

The current, I_{CE1} , is approximately the same if the coil load is placed either in the emitter or in the collector circuit, so the equation (4) can also be utilized here to get the maximum controlling value of R_B .

$$\therefore R_B = \frac{280}{23} \text{ K} \approx 12 \text{ K.}$$

The practically found value for this circuit is about 15 K Ω .

Thus, for highly conducting liquids circuit of Fig. 8 is used and for low as well as high conducting liquids circuit of Fig. 3 may be used. The diode D utilized in the transistor circuit is for the safety of the transistor.

Special Features

The circuit is having the following features to its credit: (i) it is very simple; (ii) the maximum current which passes through the liquid is only 6 μa , at 25°C for any value of the conductivity within the controlling range. Hence, the circuit may be used where electrolysis is an important factor; (iii) Taking the safe controlling value of R_B as 100 K., which corresponds to the conductivity of 10 μmho , the circuit can be used for liquids of conductivity range varying from infinity to 10 μmho i.e. it can be well utilized for tap water and aqueous solutions of (i) acids, such as hydrochloric,

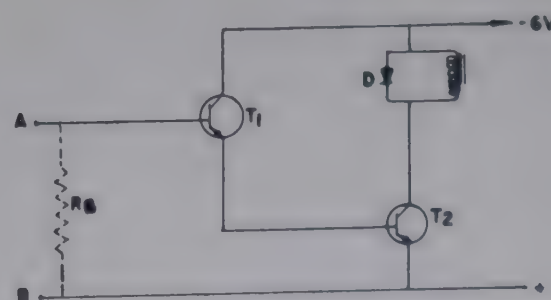


Fig. 8

sulphuric, nitric, and acetic acids, etc. (ii) bases e.g. caustic potash, soda and ammonium hydroxide, (iii) salts such as common salt, ammonium chloride, copper sulphate, ammonium nitrate, ammonium sulphate, etc.

Limitations

The action of circuit is solely based on leakage current properties of a transistor and the leakage current varies linearly with the rise or fall of temperature, so its use is limited within a certain range of temperature.

It is seen that the working temperature range of the circuit of Fig. 3 is from 10 to 40°C. Below 10°C the leakage current, I_{CE1} , is not sufficient to actuate the relay in the T_2 circuit, so below this temperature the circuit does not function. If the temperature goes above 40°C then by shorting the electrode points the relay does not go off, it means the leakage current of T_2 becomes so high that the relay still remains in the pulled-on position (T_1 also contributes to this leakage current due to the presence of r_{b1} in the R_B path).

In the given temperature range the circuit can be used upto the conductivity of water only. But if it is used for still lower conducting liquids the limiting temperature range will be from 15 to 35°C. The working temperature range of the circuit can be extended on either side by the addition of two resistors, R_1 and R_2 , in the

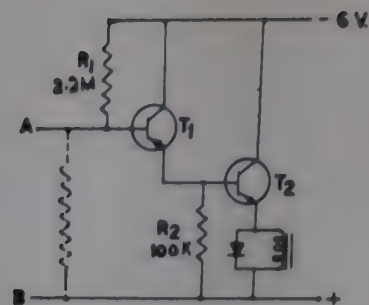


Fig. 9

circuit (see Fig. 9). R_1 pulls the lower range to about 5°C by biasing the transistor T_1 and R_2 extends the upper range to about 45°C by decreasing the leakage current of T_2 . The same can be achieved for the circuit of Fig. 8, taking $R_1 = 4.7M\Omega$ and $R_2 = 4.7K\Omega$. The increased operating temperature range is achieved at the cost of the controlling value, which is lowered mainly by the addition of R_1 .

In Fig. 9, R_2 may be replaced by a reverse biased junction diode (say 0A85) to achieve better higher temperature workable range.

Operation of the Level Switch as a Fixed Point Level Indicator and Controller: The complete circuit diagram of the level switch is shown in Fig. 10. Two transistor circuits with the two control points E_1 and E_2 and one 6 volts A.C. operated relay are utilized for the indication and control of liquid level in the liquid container,

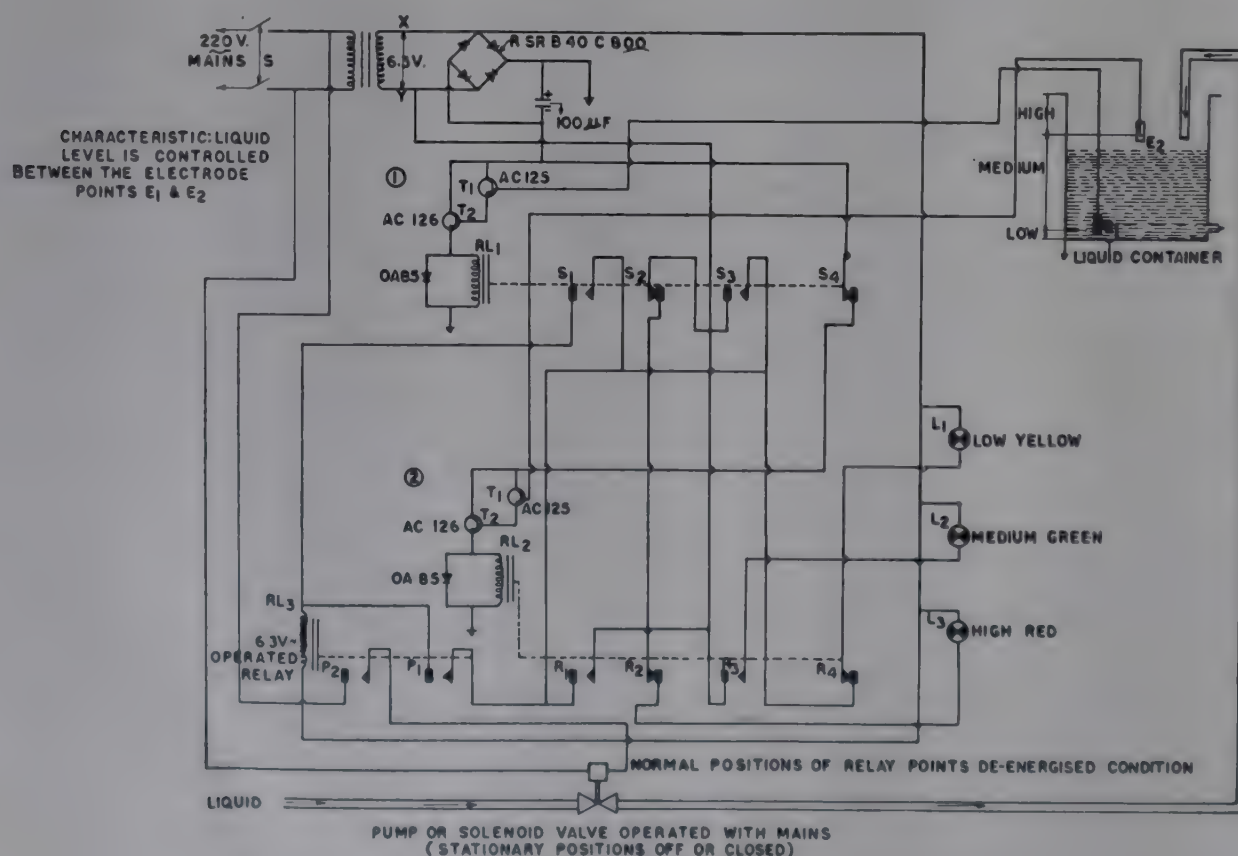


Fig. 10—Circuit Diagram of Electrode Type Level Switch

T. The D.C. power to the transistor circuits is supplied by a 6.3 volts step-down transformer, after rectification and filtration. The same 6.3 volts supply line is used for the indication lamps and the A. C. relay through the different relay switching points.

The position of the liquid level shown in the tank, T, is quite arbitrary and has no relation with the status of the circuit. The relay points represent their normal positions with the de-energized condition of the relays. The circuit action is as follows:

Assuming that there is no liquid in the tank and as the main switch S is made on the circuit (1), gets energized making the relay points S_1 and S_3 close while S_2 and S_4 are open. Due to the closing of S_3 the low level lamp is lighted up indicating that the liquid is anywhere between the bottom and the electrode E_1 and of S_1 the a.c. relay RL_3 gets energized closing the points P_1 and P_2 . The closing of P_2 gives power to the pump and liquid begins to flow through the line and tank T starts filling up with the liquid. When the liquid level touches the electrode E_1 , the circuit (1) trips and relay points come to their normal positions making the circuit (2) energized through the switch S_4 , in turn points R_1 and R_3 are closed while R_2 and R_4 opened. The opening of R_4 puts the low level lamp off and closing of R_3 makes the medium level lamp glow, indicating that the liquid level is anywhere between the points E_1 and E_2 . The pump is still on because RL_3 is getting power through the points R_1 and P_1 .

After sometime the liquid level touches E_2 making the circuit (2) off and the relay points come to their normal positions. The opening of R_3 puts off the medium level lamp and the closing of R_2 makes the high level lamp glow, indicating that the liquid level is anywhere between E_2 and the top of the tank. Since this time both R_1 and S_1 are open, RL_3 is not getting power making it de-energized and opening the points P_1 and P_2 . With the opening of P_2 , the pump is switched off and the flow of liquid into the tank stops.

From the outlet, liquid is used somewhere in the process and after sometime the level falls below E_2 , the circuit (2) trips on and again medium level lamp gets power for indication. The point R_1 is closed but both S_1 and P_1 are open; therefore RL_3 still remains in de-energized condition keeping the pump to remain off. As the liquid level falls below E_1 , circuit (1) is triggered making S_1 and S_3 to close which energizes the relay RL_3 , and again the pump gets power through P_2 , liquid starts filling the tank T. Thus, this process is repeated and liquid level is controlled between the points E_1 and E_2 . If the liquid is coming from a higher

level a solenoid valve can be used instead of the pump. In place of 6 volts A. C. relay a 230 volts relay can be used if 230 volts operating lamps are utilized.

If the tank is made up of a metal the common earthing points of the circuits must be connected to the tank body but if the container is made up of an insulating material, say a polythene or glass bottle, a separate electrode must be inserted into the container reaching upto its bottom.

Other Uses and Applications

The transistor circuit utilized for the level indication may be put in use for other applications also. Some of them are described here.

(1) In the laboratories it is found that the high temperature furnaces are cooled by the circulation of water coming from the tap. If by chance this tap water stops the inner high temperature of the furnace may melt the outer casing of the furnace, if the power to the furnace is not immediately put off. To save the life of the furnace against this unwanted irregularity in the water supply, an alarm indication must be necessary to inform immediately the worker about the failure of water supply. And this can be done very easily by inserting the control points A and B in the stream of water where the electrode points should remain in contact with water but they should be insulated with the pipe line (if it is a metallic one). Till the water circulation continues, the points A and B remain in the water stream and the relay is off but as soon as the tap water supply fails, the water level in the pipe line falls below the control points and the circuit is triggered making the off-point of the relay closed. If a 230 volts A.C.-operated bell is connected in series with the normally off-point of the relay, it rings up immediately as the water circulation breaks and the worker receives information in time about the water failure.

Since normally the points A and B remain short together and the current consumption of the circuit is approximately nil, a 6-volts dry battery can be used for the circuit for a pretty long time.

(2) The same type of the safety can be made for the small water distillation plants which are used in our laboratories daily. It was found that the heater of the evaporation chamber continues to heat the chamber even if the water circulation breaks; this undue heating diminishes the life of the distillation plants. This distillation can be made automatic by using this circuit. If the heater supply is given through the normally close points of the relay and control points are kept in the water

line of the system, the heating will continue till water is flowing through the line but as soon as the tap water stops, the circuit is triggered, making the heater circuit off. When water begins to flow through the tap, the circuit again trips, the heater gets the power and distillation continues.

(3) A large number of constant temperature baths are in use in our laboratories utilizing an on-off circuit with the electronic valves. For the economy of the space and the money this circuit can be very well utilized there.

(4) At many places it is desired to control the pressure of a gas to a particular value shown by the mercury or water manometer. In such a case, point B can be connected to the lowest end of the manometer and A can be made variable in one of the limbs of the manometer and adjusted to any pressure. The normally off-contact point of the relay should be connected to the vacuum pump through the mains supply. As the liquid level reaches the point A, the relay circuit is triggered and the supply to the pump is cut off. When the pressure falls below the adjusted value, the pump starts and the process is thus repeated, pressure being maintained to a particular value.

(5) The same circuit can also be utilized for the safety of the lockers, quarters, laboratories, etc. against thieves by adjusting the control points A and B on inner side of the door which in turn can be adjusted in shorted position when it is closed. As soon as the door is opened by an undesirable person, the circuit breaks and ringing of a bell will inform about the unwanted opening of the door. In such a case, the desired person must have a separate key arrangement to put the circuit off from outside when he desires to enter the room.

Acknowledgement

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Mixture of CuO-ZnO, CuO-Al₂O₃ and CuO-SiO₂ have been subjected to heat treatment. Evidence of large diffusion of Cu²⁺ in ZnO has been found by ESR and magnetic studies. Cu²⁺ diffuses much less in SiO₂, and the least in Al₂O₃.

A Comparative Study of the Behaviour of Cupric Oxide in Presence of Zinc Oxide, Alumina and Silica

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Introduction

Supported copper catalysts have been put into use to catalyse numerous reactions. Different materials, particularly oxides like zinc oxide, alumina and silica, have been used as the substrate. In catalysing the water gas shift reaction at comparatively lower temperatures, cupric oxide is specifically used in combination with zinc oxide. The specificity of the combination deserves attention. It has been generally held that electron exchange between the supported phase and the substrate¹ is important in the action of such catalysts. In the present communication, a comparative study of ESR spectra of mixtures of CuO-ZnO, CuO-Al₂O₃ and CuO-SiO₂ preheated to different temperatures has been undertaken to find out any preferential change in the system that can be correlated with the catalytic activity.

Experimental

Equimolar proportions of the oxides were intimately mixed and different batches were subjected to heat treatment for four hours at 250, 400, 600, 800 and 940°C. The maximum was chosen to avoid decomposition of cupric oxide. The heating was done in platinum crucibles in an electric furnace. After cooling, the samples were tested by x-ray diffraction for any phase change produced by the heating.

The ESR spectra were recorded on a Bruker model

B-ER 402 X-band ESR spectrometer, with proton resonance field marking.

The room temperature magnetic susceptibilities were measured on a Curie-type magnetic balance described in a previous paper².

Results

The ESR spectra are reproduced in Fig. 1. The different groups of absorption lines are marked with numerical indices for reference. The changes in the ESR spectra began to appear at 600°C; therefore only those spectra are given where the samples were preheated to 600°C and above. The single oxides did not give rise to any strong signal on heat treatment.

The variation of room temperature mass susceptibility with preheating temperature is shown in Fig. 2. The curve for CuO+Al₂O₃ was not included, because the Al₂O₃ was found to contain impurities in traces. No new phase was found by X-ray diffraction.

Discussions

The most conspicuous feature of the spectra is that while the singly-heated oxides give rise to practically no ESR signal, the mixed oxides have produced prominent signals after being heated. This indicates that there must be some sort of interaction occurring between cupric oxide and the other components at elevated temperatures. Since x-ray examination had failed to

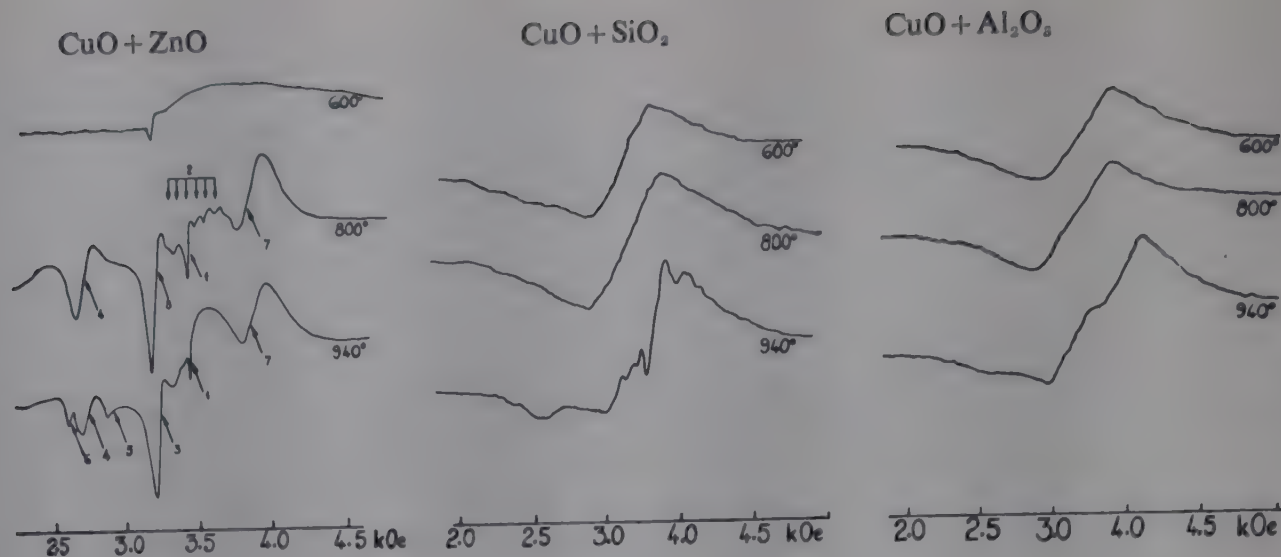


Fig. 1—ESR Spectra of Mixtures

detect any new bulk phase, the interaction zone must be limited to the region of contact.

Cupric oxide is antiferromagnetic³, having a Néel temperature of 150°C, exhibiting only a very feeble paramagnetism⁴ below this temperature. This explains the origin of the broad weak signal, which is present in all the spectra.

The CuO-ZnO system shows the earliest formation of a new phase, as evidenced by the sharp line which appears in the spectrum of the sample heated to 600°C.

ZnO is known to lose oxygen on heating, creating vacancies in the lattice that serve to trap electrons and producing F-centres¹. Simultaneously, Zn^{+} ions⁵ are also formed which migrate to interstitial positions. In the spectrum of the sample heated to 800°C, two sets of lines, marked 1 and 2, are observed—the first, a single narrow line, with $g=2.0019$ and the second, a group of six lines having a line spacing of about 66 gauss and a mean $g=1.9953$. The close proximity of the g -values to the g -factor for free electrons indicate that the lines originate from the F-centre and/or the Zn^{+} centre. However, the Zn^{+} centre seems to be the more probable source because the six hyperfine lines can be produced only by the interaction with the Zn^{67} nuclear species having nuclear spin of $5/2$ units and a natural abundance of 4.12 per cent. The slight variation in the g -values can be attributed to the isotope-shift effect. Had the signals been due to the F-centre, the mean g -value of the group 2 would have coincided with that of 1.

Moreover, the rather large separation between the six component lines, when considered with the small nuclear moment of the Zn^{67} nucleus, indicates a large charge density of the unpaired electron at the nucleus,

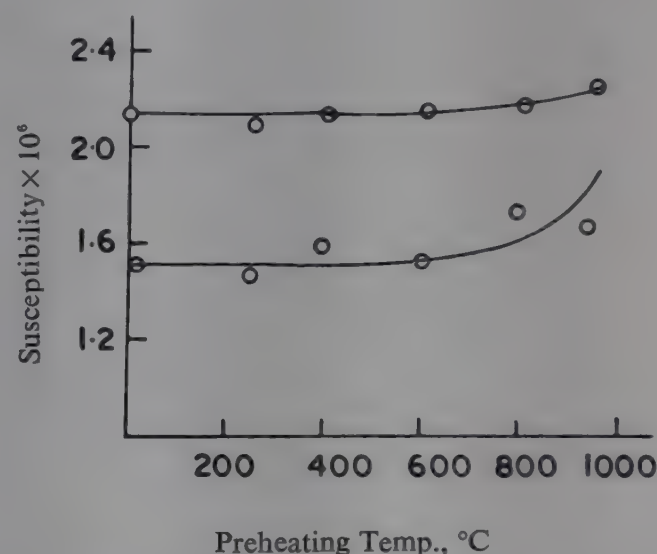


Fig. 2—Variation of Room Temperature Mass Susceptibility with Preheating Temperature

or in other words, an unpaired s-electron is indicated. This also supports the Zn^{+} hypothesis.

The obliteration of the hyperfine structure at 940°C may indicate the formation of Zn atoms on migration of the interstitial Zn^{+} ions to the surface¹.

The lines 3,4,5 and 6 are originating from copper ions forming a boundary phase, which can only arise from diffusion of copper ions in the ZnO lattice. The copper ion can go either to substitution positions or to the interstitial positions or both. The reason why the bulk copper oxide phase does not produce any sharp signal has already been stated. The four lines perhaps arise from the $g_{\parallel}$ and $g_{\perp}$ values of the cupric ions at the two non-equivalent positions. The line 7 could not be interpreted.

In case of the CuO-SiO₂ mixture, the boundary phase appears only in the sample heated to 940°C, and in the CuO-Al₂O₃ mixture, there is no trace of a boundary phase having cupric ions in a dispersed state.

The pattern of change in magnetic susceptibility also confirms the picture arrived at from the study of ESR spectra. In the CuO-ZnO mixture, where the largest amount of dispersed copper has entered the substrate, there is a substantial increase in magnetic susceptibility with increasing preheating temperature. The change is less noticeable in the case of CuO-SiO₂ mixture, and the least in the CuO-Al₂O₃ system.

Conclusion

In the present investigation, the areas of contact of CuO with the diamagnetic bases have been intentionally kept very poor by taking mechanical mixtures of the oxides. In case the cupric oxide is formed as a layer by treating the substrate with cupric nitrate solution and subsequent curing, the area of contact will be much

larger, favouring a greater degree of diffusion of copper ions. But the results obtained here clearly show that cupric ions preferentially diffuse more in ZnO, as compared to the two other bases. The reason for this may be that the ionic radius of Cu²⁺ is nearer that of Zn²⁺ than of either Si⁴⁺ or Al³⁺. The easy diffusibility may be a factor in determining the catalytic activity.

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The thermal decomposition of CrO₃ under vacuum has been studied by ESR and magnetic susceptibility methods. The main difference from the usual decomposition route observed under oxygen atmosphere appears to be the absence of the Cr₂O₅ phase. Tentative interpretation of observed ESR spectra has been given.

Magnetic Studies on the Thermal Decomposition of Chromium Trioxide under Vacuo

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Chromium oxides have been widely used as catalyst for diverse types of reactions which can be grouped in two main classes, namely, polymerisation reactions^{1,2} and oxidation reactions^{3,5}, the latter being the more important in the field of inorganic chemistry. It is well-known that the active form of the catalyst is often quite different from the phase originally introduced in the reaction vessel, the final form depending mainly on the conditions prevailing there. For instance in the catalytic oxidation reactions the ambient condition is necessarily oxygen-rich. The decomposition of the higher oxides of chromium, e.g. CrO₃ has been well-

studied^{6,7,8} under oxygen-rich conditions and under high pressure, so that the criteria for the stability of the catalytically active phase under these conditions are also well established.

It would be worthwhile to know the mode of decomposition of the higher oxides of chromium under low pressure and oxygen-lean conditions, so that the knowledge gained may be employed in cases where reactions demand similar ambient conditions.

The tools of study employed here are ESR spectrometry, magnetic susceptibility determination and x-ray

diffraction. X-ray diffraction serves to identify the major phases. CrO_3 is diamagnetic and Cr_2O_3 is antiferromagnetic at room temperature, whereas CrO_2 is ferromagnetic with a Curie point at 400°K (127°C), the two other phases Cr_3O_8 and Cr_2O_5 being paramagnetic⁹ at the room temperature and above though they may show antiferromagnetism at lower temperatures. Therefore magnetic susceptibility measurement and observation of Curie point transition should give a sensitive test for the formation of the ferromagnetic CrO_2 phase and ESR should be able to distinguish between the different paramagnetic phases.

Experimental

Analytically pure grade reagent CrO_3 was used in the experiments as the starting material. Different batches were heated to the different temperatures, viz., 175, 300, 400 and 500°C under a vacuum of 10^{-2} torr, kept for 24 hrs. and then gradually cooled down under vacuo. It may be assumed that any reversible transformation cannot take place under such conditions, because the oxygen liberated on decomposition would be continuously removed.

The heating was done in an electric resistance heating furnace comprising a silica tube closed at one end, over which the heating coil was wound. The vacuum pump was connected to the open end. The furnace was calibrated by using a chromel-alumel thermocouple under the vacuum, noting the temperatures corresponding to various settings of the variable auto-transformer which controlled the heating current.

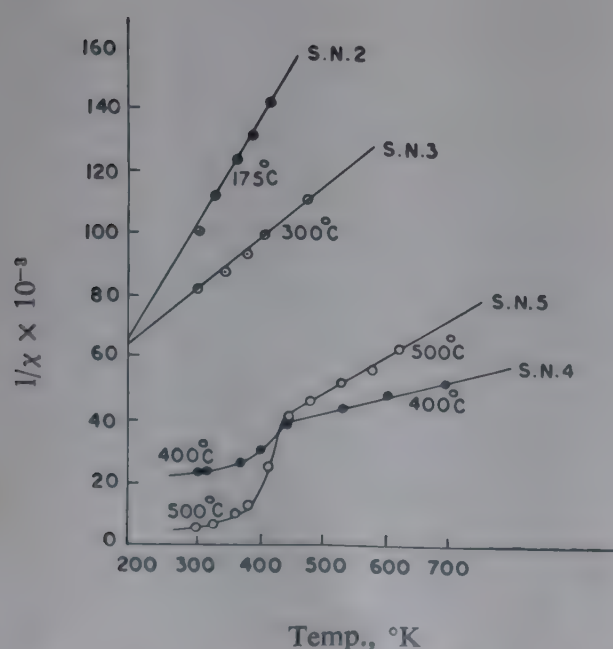


Fig. 1— $1/\chi$ vs T Curves for Reduced CrO_3 Samples (Reducing Temperature is shown in Diagram)

Magnetic susceptibility measurements were made on a Curie-type susceptibility balance with an electrodynamic balancing system similar to one described by Pandey¹⁰ et al. ESR spectra were recorded on a x-band spectrometer from Bruker-Physik A.G. (Model B-ER 402), using a TE_{102} mode rectangular cavity. Polycrystalline D.P.P.H. was used to standardise the spectrometer. The magnetic field strength was measured by a proton resonance gaussmeter.

Results

On heating, the physical appearance of the sample changed. The heat treatment data, sample colour, the corresponding major phase compositions as found out by x-ray diffraction studies and the room temperature mass susceptibility data are given in Table 1.

TABLE 1

Sample No.	Temperature of heat treatment	Colour	Major Phase	Mass Susceptibility, C.G.S. Units/g
1.	Untreated	Brown	CrO_3	0.55×10^{-6}
2.	175°C	Black	CrO_3 + Trace Cr_3O_8	1.10×10^{-6}
3.	300°C	Dark Brown	Cr_3O_8 + Unknown phase in traces	11.84×10^{-6}
4.	400°C	Green	Cr_2O_3	30.03×10^{-6}
5.	500°C	Green	Cr_2O_3	145.50×10^{-6}

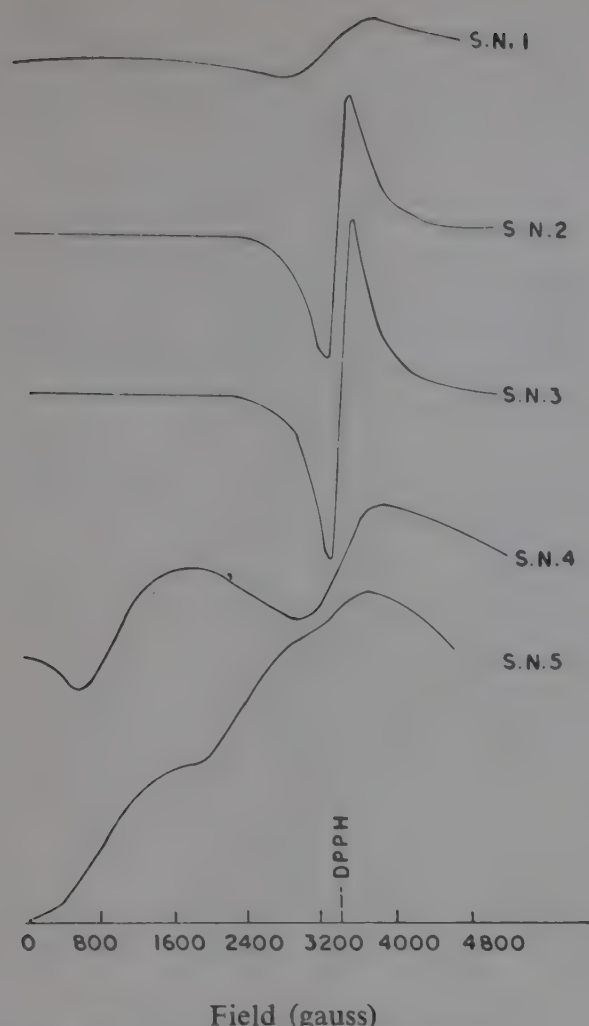
The temperature variation of susceptibility is shown in

Fig. 1, where $\frac{1}{\chi}$ the inverse of mass susceptibility has

been plotted against the absolute temperature (T). The sample nos. as per Table 1, are shown against the appropriate curves. It may be noted that the samples no. 2 and 3 show normal paramagnetic behaviour of a substance obeying the Curie-Weiss law, whereas in samples no. 4 and 5, a distinct Curie point transition is present. The ESR spectra are reproduced in Fig. 2.

Discussion

The trioxide CrO_3 , though expected to be diamagnetic from its d^0 configuration, actually shows a feeble paramagnetism as confirmed in Table 1, and also from the observed ESR signal. The susceptibility was found to be temperature independent by Tilk and Klemn¹¹, thus showing it to be a second order effect, arising from the interaction of the ground state level with the higher



Field (gauss)
Fig. 2—ESR Spectra of Samples

excited levels. However, the appearance of a broad ESR signal indicates that some other phase is also present, if only in trace amounts.

Between the d^0 state CrO_3 and the d^4 state CrO_2 , generally Cr_3O_8 and Cr_2O_5 are formed as shown by Kubota⁹. From the x-ray analysis Cr_2O_5 was found to be absent in both samples 2 and 3. In sample 3, some other phase was found in traces whose line pattern did not bear any resemblance with that of any known oxide of chromium.

From the ESR spectra also it appears that the phase Cr_2O_5 had not formed during the heating. It is expected to give an ESR absorption line of about 50 gauss half-line width¹², whereas the observed half-line widths for the samples 2 and 3 are of the order of 250 gauss. The comparative narrowness of the Cr_2O_5 absorption line would enhance the detection sensitivity, and it may be concluded, that even if it had formed the amount of the phase must have been below the detection limit of the instrument.

From x-ray analysis, the major phase in sample No. 4 is Cr_2O_3 , in which CrO_2 has started to form, as found from the susceptibility temperature curve. The ESR signal in the sample 4 therefore may be taken to be due to Cr^{3+} ions in some defect state of Cr_2O_3 . In sample 5, where the amount of CrO_2 has increased considerably as shown by its room temperature susceptibility, which jumps from 30×10^{-6} to 145×10^{-6} , a new ESR absorption line has appeared between the two lines obtained with sample No. 4. Obviously, the concentration of this phase is now sufficient for ESR detection though it is still below the detection limit of x-rays.

The occurrence of the two ESR absorption lines in sample 4 may be interpreted in terms of a zero field splitting of the $^4A_{2g}$ ground term of Cr^{3+} ion under axially distorted octahedral bonding. The splitting scheme has been shown in Fig. 3, the resonance conditions being $h\nu = g\beta H_1 + \delta = g\beta H_3 - \delta$ for the $M_s = -\frac{1}{2} \rightarrow \frac{1}{2}$, $\frac{1}{2} \rightarrow \frac{3}{2}$ and $-\frac{3}{2} \rightarrow -\frac{1}{2}$ respectively. The zero field splitting δ is calculated to be 0.238 cm^{-1} . The third ESR line, therefore, is expected to come at 6080 gauss, which was beyond the observation limit.

In the case of CrO_2 , zero field splitting scheme of the three-fold degenerate spin level of Cr^{4+} , by the action of a ligand field with an axial symmetry is shown in

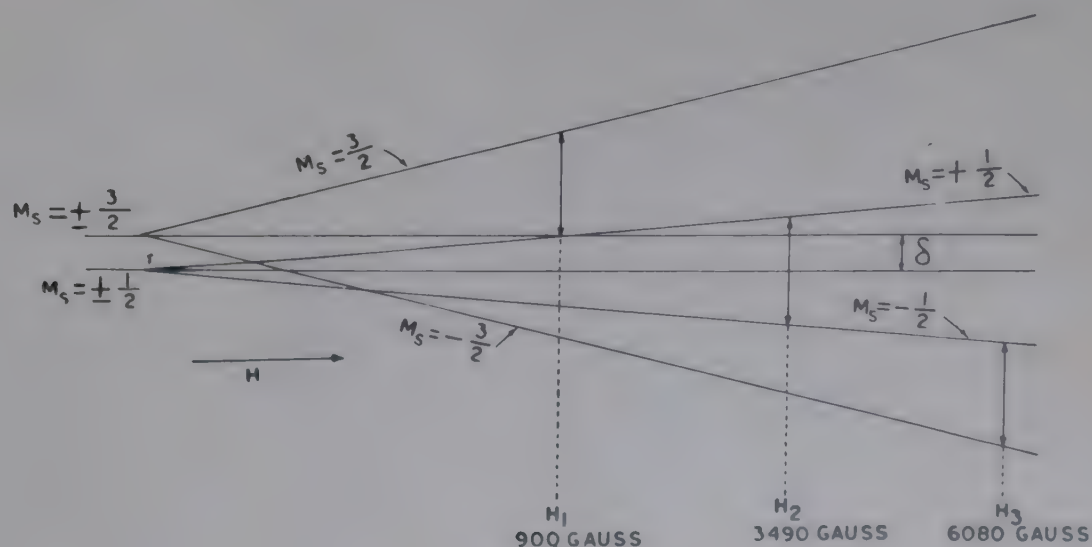


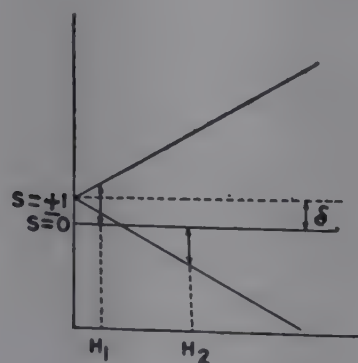
Fig. 3—Level Splitting Scheme for Cr^{3+} Ion

Fig. 4 for which the transitions $M_s=0 \rightarrow \pm 1$ occur at $h\nu = g\beta H \pm \delta$. The splitting is calculated to be 0.0659 cm^{-1} . H_1 and H_2 are taken as 3525 gauss and 2325 gauss from the spectra of sample No. 5. It seems that ESR line at 3490 gauss due to Cr^{3+} and one at 3525 gauss due to Cr^{4+} are overlapping in the spectrum of sample No. 5 and are unresolved. Thus the ESR spectra of sample No. 5 gives a clear cut indication of the presence of CrO_2 with some defect state of Cr_2O_3 .

A prolonged heating or a higher temperature would certainly have completed the conversion of Cr_2O_3 .

Conclusions

From the results, the main course of decomposition of CrO_3 heated in vacuo is $\text{CrO}_3 \rightarrow \text{Cr}_3\text{O}_8 \rightarrow \text{Cr}_2\text{O}_3$, with small amounts of other phases like CrO_2 and an unidentified phase forming at different temperature ranges. The phase Cr_2O_5 is not forming at all. By contrast the course of decomposition under high ambient oxygen pressure covers many more steps including the Cr_2O_5 phase.



Magnetic Field, H

Fig. 4—Level Splitting Scheme for Cr^{4+} Ion

Catalytic reactions, in which Cr^{5+} is the active catalyst phase cannot therefore take place under vacuum or oxygen-free conditions.

Acknowledgement

Thanks are due to Mr. M. Mishra for the X-ray identification work. The authors are grateful to Dr. B. K. Banerjee, Additional Superintendent, Physical Research Wing, for encouragement.

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The Adsorption of Fe^{59} in haematite, Zn^{65} in sphalerite, and Ba^{133} in barite has been studied as a function of contact time and pH. A rapid adsorption has been marked at the beginning, which falls off sharply after attaining the maximum value. The adsorption has also been found to increase with the increase of pH of the tracer solution. The results obtained for Fe^{59} , Zn^{65} and Ba^{133} have been compared.

Adsorption of Radiotracers by Mineral Particles

Part I: Effect of Contact Time and pH on Adsorption

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Introduction

Adsorption is one of the most widely used surface phenomena. Basically, it is of two types—physical adsorption and chemisorption. The former is mainly non-specific whereas chemisorption shows a high degree of selectivity. The adsorptions of either type—both from gases and solutions—have a large field of application in industry. Recently, the adsorptions of radiotracers have also been investigated for radioactivation of mineral particles, tracing the course of different minerals in flotation studies¹, concentration of carrier-free radioisotopes, in aqueous corrosion problems², etc.

The present study is mainly for investigation of various factors which influence the adsorption of radiotracers in solutions by mineral particles. Here the adsorption as a function of contact time and pH has been discussed.

Experimental

The adsorbents, viz haematite (Fe_2O_3 containing 77 per cent of Fe), sphalerite (ZnS having 55 per cent of Zn) and barite (BaSO_4 having 58 per cent of Ba), were crushed and sieved, and the particles having an average size around 200 mesh (B.S.S.) were chosen. Fe^{59} , Zn^{65} , and Ba^{133} were taken as tracers, which are all gamma-emitters of considerable long half-life compared to the duration of the experiment. Therefore, no correction for radio-active decay of the tracers became necessary. Stock solutions were prepared with the tracers having pH values 2, 4 and 6. The strength of each solution was 10^{-2}M . The pH values of the solutions were adjusted

with caustic soda and sulphuric acid and were measured with standard calomel and glass electrodes. Specific activities of the stock solutions were $39 \mu\text{Ci/ml}$ for Fe^{59} , and $100 \mu\text{Ci/ml}$ for both of Zn^{65} and Ba^{133} . From the stock solutions, 3 ml. was taken in separate beakers against each pH value and 0.2 gr. of the adsorbent mineral was added to respective tracer solutions. The contact time was varied upto 15 hours in four different stages, viz. 2.5, 5, 10 and 15 hr. The exposures were given at room temperature and at atmospheric pressure. After each contact period, the adsorbent and adsorbate mixture was transferred from the beaker to a vacuum filtration unit consisting of Buchner funnel, Whatman No. 40 ashless filter paper, water pump, etc. After filtration, the residue was washed thoroughly in each case with warm distilled water four to five times, till the filtrate was free of any activity. The filter paper with thinly-coated precipitate was then transferred to a suitable stainless steel planchet and dried by means of I.R. lamp.

The activity of the precipitate was measured by means of a single channel gamma-ray spectrometer with $1'' \times 1''$ NaI(Tl) crystal mounted on RCA 6199 Photomultiplier Tube coupled with a Decade scaler. The source planchets were always placed for activity measurements at the best feasible geometry. Proper collimation was done with annular lead rings. The spectrometer was calibrated with the standard gamma emitters of suitable energy ranges and the adsorbed activities for iron, zinc and barium were measured in terms of the count rates at their respective photopeaks.

Results and Discussion

From a study of the adsorption of Fe^{59} by haematite against contact time [Figs. 1(A&B)], it is found that the former is very rapid at the beginning and becomes maximum for a contact period of about 5 hr, after which there is a sharp fall and finally it tends to attain a saturated value. Adsorption is found to increase fairly with pH of the tracer solution (Fig. 1B).

Figs. 2 (A & B) represent the adsorption of Zn^{65} by sphalerite against contact time and pH respectively. Here a marked difference is noticed in results relative to those for Fe^{59} . The adsorption of Zn^{65} is found much less compared to the swift uptake of Fe^{59} in the respective minerals. An irregular variation in adsorbed activity has also been found with a tendency of maximum adsorption nearabout 10 hours of contact. However, a more or less uniform increase of adsorption with pH has been marked.

The uptake of Ba^{133} with contact time and pH of tracer solution has been found almost similar to that of Fe^{59} , but slightly lesser in magnitude [Figs. 3 (A & B).]

An analysis of results for Fe^{59} , Zn^{65} and Ba^{133} indicates clearly that in each case there is an initial rapid uptake for the tracers from solution by the mineral particles which finally decreases and tends to be saturated after attaining some maximum value. This initial rapid adsorption may be attributed to the availability of fresh

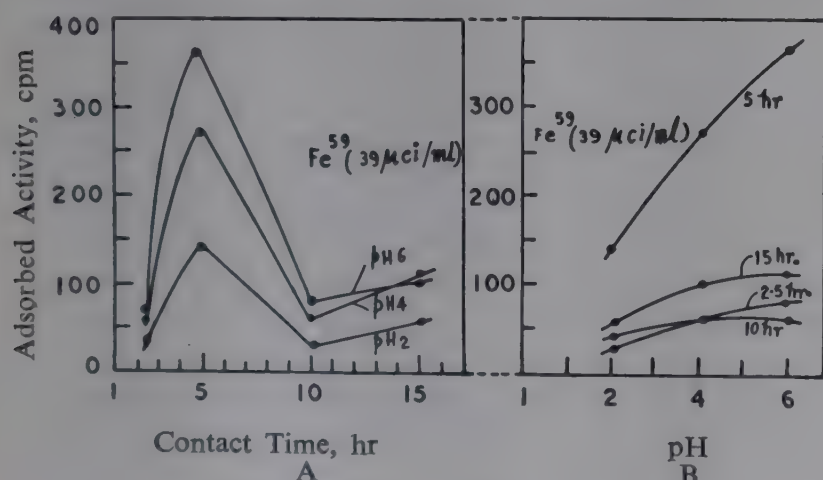


Fig. 1—Adsorption of Fe^{59} on Haematite

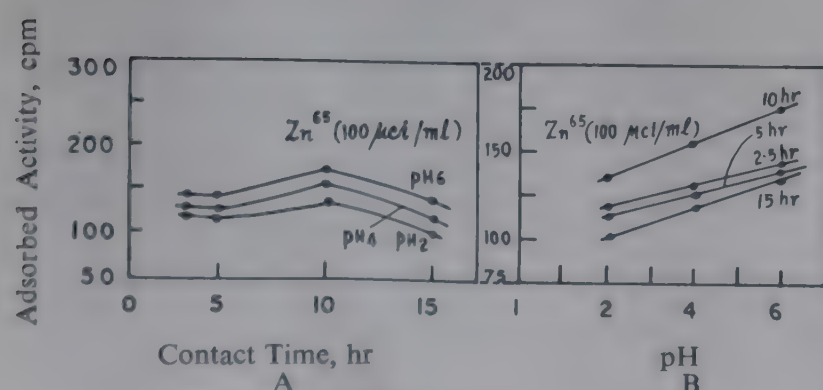


Fig. 2—Adsorption of Zn^{65} on Sphalerite

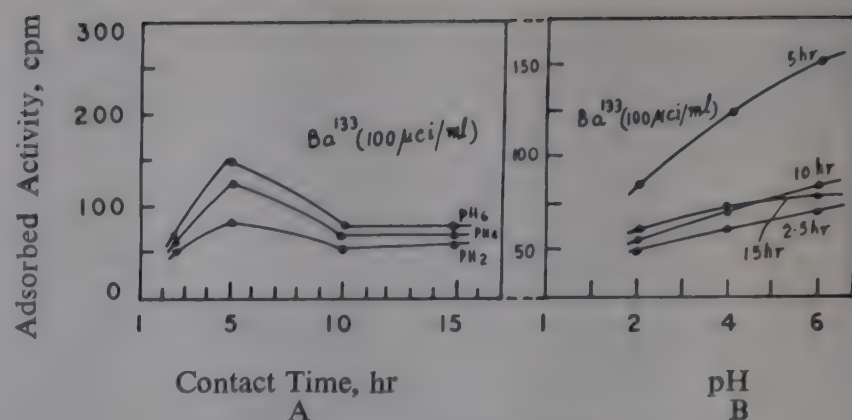


Fig. 3—Adsorption of Ba^{133} on Barite

reception surfaces of mineral particles at the beginning of experiment. With the increase of contact period an equilibrium is gradually reached between the solution concentration of tracer ions and those on the particle surfaces. As a result, the adsorption also becomes necessarily decreased.

With the same amount of adsorbent particles, viz. 0.2 g., Fe^{59} ($39 \mu\text{Ci/ml}$) has been found relatively more adsorbed than Zn^{65} and Ba^{133} ($100 \mu\text{Ci/ml}$ each) even at lower concentration of tracer solution. This may be due to the fact that percentage of iron in haematite used has been found to be 77 per cent in comparison to 55 per cent of zinc in sphalerite and 58 per cent of barium in barite. Thus, the effective mineral content being maximum in haematite, the corresponding tracer uptake is also maximum because of relatively more available receptive surfaces.

It has been found that adsorption increases fairly with the pH of tracer solutions. The lower adsorption rate at the lower pH values may be explained, in accordance with Veljkovic³ et al due to some changes on the receptive particle surface of adsorbents caused by the high acidity of the tracer solutions. However, the value of pH required for saturation of adsorption has not been reached because of the possibility of hydroxide precipitation at higher pH values. Therefore, adsorption of radio-tracers in solutions is possible provided there is an adequate solubility to prevent precipitation at the pH involved.

Acknowledgement

The authors are thankful to their colleague, Sri P. Das, for assistance in the preparation of mineral samples and in filtration work.

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An apparatus for measuring thermal conductivity of small oxide and catalyst pellets at medium temperatures has been developed by utilizing the heat flow comparator method. The performance tests have been carried out with the pellets of copper and zinc oxide powders pressed to different bulk densities as well as one commercial asbestos board specimen of known thermal conductivity. It has been observed that at similar bulk density and mean temperature, the thermal conductivity of these samples are in good agreement with the reported values. Thermal conductivity of these samples as well as one industrial catalyst of known bulk density (CO-conversion ZnO/CuO type), determined at different temperatures up to 150°C., has been found to increase with temperature. Furthermore, the effect of temperature on the thermal conductivity of the catalyst sample is similar to that of ZnO pellet.

An Apparatus for Measuring Thermal Conductivity of Small Oxide and Catalyst Pellets at Medium Temperature

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Heat transfer data are being utilized by design engineers since long, for choosing and application of suitable insulation for reaction chambers, pipes, etc. and for deciding an adequate thermal power requirement for specific reactions. It has been found¹⁻² that to get the maximum activity of catalysts during reactions, the optimum conditions should be maintained rigidly and that an exact knowledge of temperature variation throughout the catalyst pellet is an important factor in elucidating such an optimum state. Thermal conductivity of oxides and catalyst pellets has been measured by some workers³⁻⁷, using different methods and apparatus. The instrumental design differs primarily due to the fact that they are very much dependent on the shape, size and conductivity of the samples⁸⁻¹².

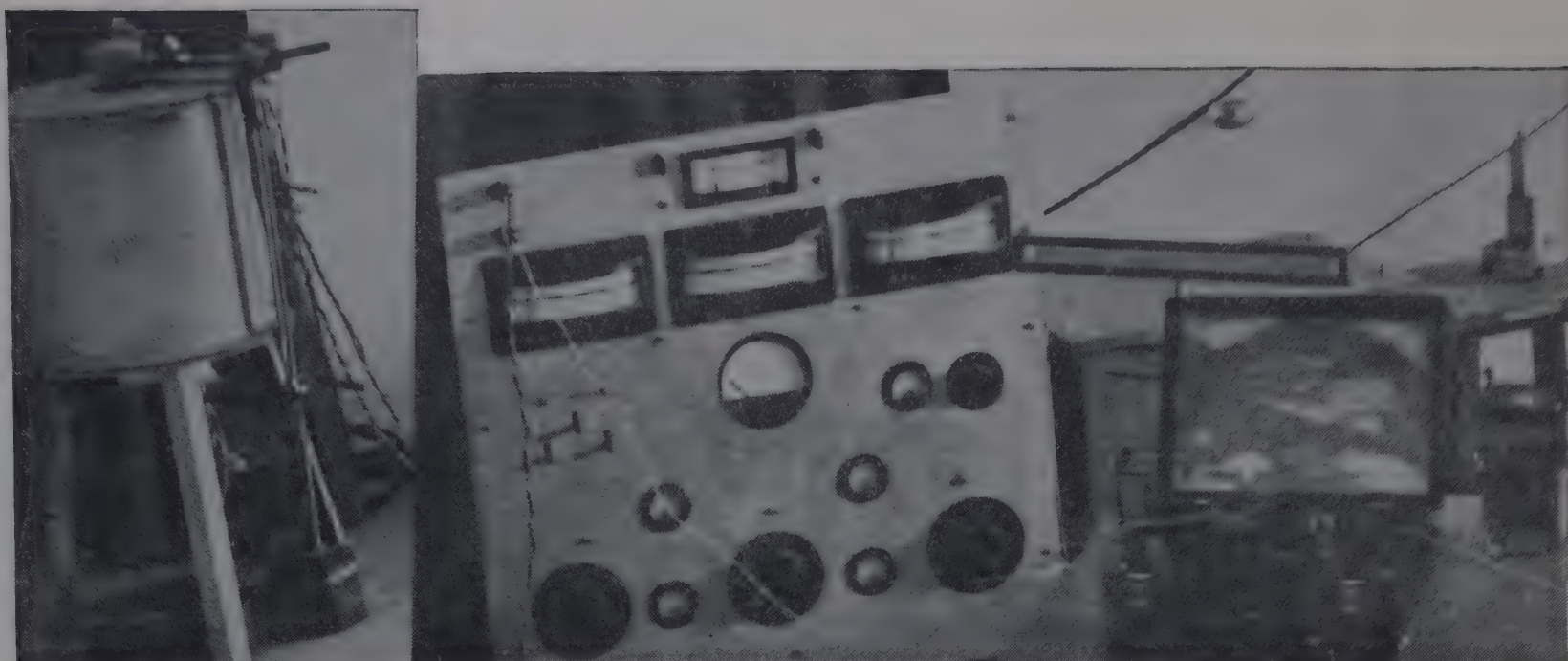
Among the methods the heat flow comparator one has been found to be most suitable for measuring thermal conductivity of small samples. Francl & Kingery⁷ used it for highly pressed ceramic oxides of 1 in. cube size, the porosity of which is usually very small. The procedure comprises in establishing an uniform heat flow through two or more samples, measuring its temperature drop and heat flow and from the known thermal conductivity data of a standard non-porous material, e.g. lead or silver, the thermal conductivity of an unknown sample can be calculated. Usually catalyst pellets are porous materials as pores are necessary because they determine to a large extent the catalytic

activity. In case of catalyst pellets which are porous and whose pellet size is very small, complication arises for achieving a steady state with such instruments utilizing comparative method. Again thermal conductivity of such pellets as determined by comparing with a standard non-porous material will be erroneous. For an accurate determination, an instrument is necessary which can be standardized with similar porous materials under identical operating conditions.

An attempt has been made here to develop a suitable apparatus for measuring thermal conductivity of very small porous oxide and catalyst pellets at medium temperatures based on heat flow comparator method in which the specimen is placed in-between two metallic bars of the same cross-sectional dimension as the specimen¹³.

Apparatus

The apparatus consisted of a test chamber, control panel of heaters and temperature measuring equipment (Fig. 1). The test chamber had two cast iron bars of 10 mm. diam, 35 cm. length of known thermal conductivity, each having two thermocouples—one near the interface and the other at a distance of 70.6 mm. from it. Thermocouples were made of 24 SWG chromel/alumel wires; the heater fitted at the outer end of one bar was made from a 10 cm. long, 2.5 cm i.d. sillimanite tube, wound with 22 SWG Kanthal wire. A separately



A—Test Chamber

B—Control Panel

Fig. 1—Apparatus for Measuring Thermal Conductivity of Small Samples of Oxide and Catalyst Pellets at Medium Temperatures.

heated guard cylinder (F), also of sillimanite, of 10 cm i.d. and 30 cm. length, with three separate heater windings, was provided (Fig. 2), and a copper guard cylinder (E) with three 24 SWG chromel/alumel thermocouples attached at places corresponding to the above three heater windings was placed inside, for automatic control of heaters. Insulating bricks were placed round the guard cylinder to reduce the lateral flow of heat. A compressed spring was used for applying pressure on the specimen, through a mild steel tube fitted above the test chamber (Fig. 2). The lower bar was supported over a stout platform, with proper heat insulation using clamps. Temperature-measuring equipment consisted of a precision potentiometer with its accessories and a selector switch of a very low resistance.

The specimen pellets were made in a die, which produced cylindrical pellets of 10 mm. o.d. and 10 mm. length.

Method

The specimen pellet of a specified size was placed between the two cast iron bars and the outer end of the lower bar was electrically heated. The heater was fed from 220 volts, stabilized A.C. mains, through an ammeter and auto-transformer. The outer end of the upper bar was air-cooled. The heaters of the heated guard cylinder were fed from 220 volts, A.C. mains, through auto-transformers and pyrometric temperature controllers. The e.m.f. developed in the thermocouples attached to copper guard cylinder was fed to these controllers, for automatic temperature control. The temperatures

of the previously calibrated thermocouples T_1 , T_2 , T_3 and T_4 were measured by null method with a previously calibrated potentiometer. Time required to attain steady state was about 4 hrs. Heat flow through a porous pellet at steady state was as follows:

$$q_1 = \lambda_1 A \frac{t_1 - t_2}{d_1} \text{ and } q_2 = \lambda_2 A \frac{t_3 - t_4}{d_2}$$

$$\& q_s = \lambda_s A \frac{t_2 - t_3}{d_s} = \frac{q_1 + q_2}{2}$$

q_1 , q_2 and q_s are quantities of heat flowing through lower and upper bar as well as sample of thermal conductivity λ_1 , λ_2 and λ_s respectively.

and, when $d_1 = d_2 = d$ and $\lambda_1 = \lambda_2 = \lambda$

$$q_s = \frac{\lambda A}{2d} (t_1 - t_2 + t_3 - t_4) = \frac{\lambda_s A}{d_s} (t_2 - t_3)$$

$$\therefore \lambda_s = \frac{\lambda d_s}{2d} \left(\frac{t_1 - t_4}{t_2 - t_3} - 1 \right) \quad \dots (1)$$

Equation (1) was utilized for calculating thermal conductivity of the pellet,

where, λ_s = Thermal conductivity of the specimen pellet,

d_s = Length of the specimen pellet,

λ = Thermal conductivity of cast iron bars,

d = Distance between t_1 and t_2 or t_3 and t_4 (70.6 mm).

$t_1, t_2, t_3 \& t_4$ | =Temperature of thermocouples T_1, T_2, T_3 and T_4 respectively.

A cast iron bar (with 3 per cent carbon) of a known thermal conductivity was used. The variation of thermal conductivity of this bar with temperature is shown in Fig. 3¹⁵. The thermal conductivity of the specimen was calculated by taking the conductivity value of the bar at the particular temperature. The specific test temperatures were the averages of these of the cold and hot faces of the specimens, recorded just above and below

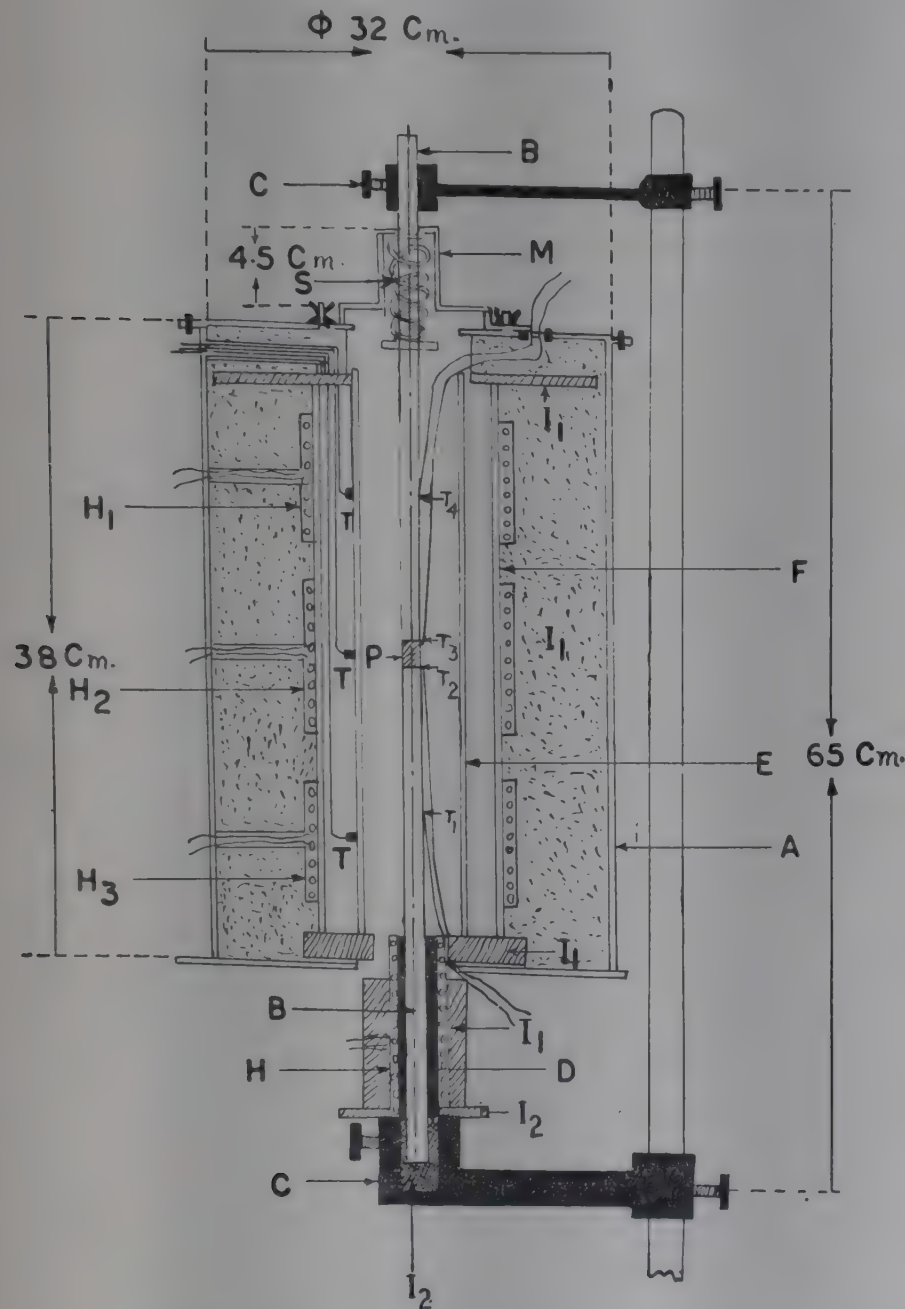


Fig. 2—Design of the Test Chamber of the Thermal Conductivity Apparatus

- | | |
|---|---|
| A—Furnace Housing | I ₃ —Asbestos Mill Board |
| B—Cast Iron Bar | M—Mild Steel Tube |
| C—Clamp | P—Specimen Pellet |
| D—Thin Mica Flakes | S—Spring |
| E—Copper Guard Cylinder | T ₁ , T ₂ , T ₃ , T ₄ } Thermocouples |
| F—Heated Guard Cylinder | |
| H, H ₁ , H ₂ & H ₃ —Heater | |
| I ₁ —Insulating Bricks | |

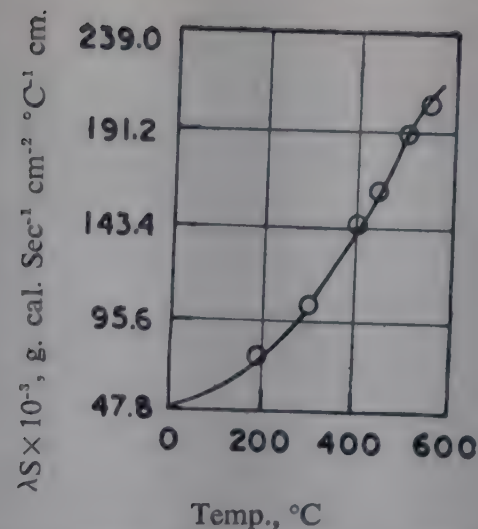


Fig. 3—Thermal Conductivity of the Cast Iron Bar at Different Temperatures

the test specimens respectively. In this experimental set-up the differential temperatures over the specimens were maintained within 25 to 50°C. These temperatures were determined when the steady state was attained. The temperature differential under a particular steady state condition was reproducible within ± 0.5 per cent.

The performance tests were performed with the pellets of copper and zinc oxide powders (A. R. grade) pressed to different bulk densities as well as one commercial asbestos board specimen. The variation of thermal conductivity of the pellets with their bulk density at a particular temperature is shown in Fig. 4. The thermal conductivity of these specimens at similar bulk density and mean temperature has been compared with the reported values (Table 1). Thermal conductivity of these samples as well as one industrial catalyst sample (CO-conversion type with CuO 20 and ZnO 80 per cent) having a particular bulk density was also measured at different temperatures upto 150°C. The variation of their thermal conductivity with temperature is shown in Fig. 5.

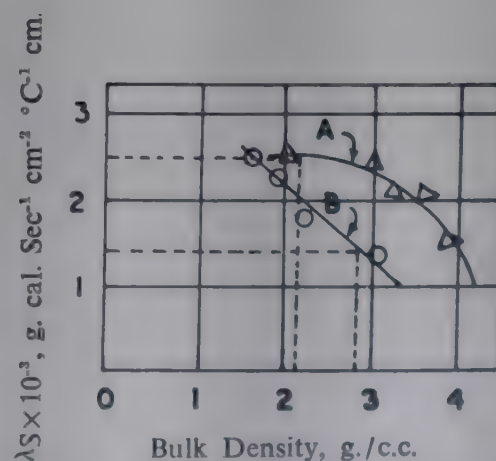


Fig. 4—Variation of the Thermal Conductivity of Pellets with their Bulk Density
A— CuO at 45°C; B— ZnO at 50°C

TABLE 1—OBSERVED AND REPORTED THERMAL CONDUCTIVITY VALUE OF SOME OXIDE AND CATALYST PELLETS

Sl. No.	Specimen	Observed Value			Reported Value		
		$\lambda \times 10^3$ g. cal, sec ⁻¹ cm ⁻² , °C ⁻¹ , cm.	T, °C	D, gm/cc	$\lambda \times 10^3$ g. cal, sec ⁻¹ cm ⁻² , °C ⁻¹ , cm.	T, °C	D, g./cc
1.	Copper Oxide (Pressed Powder)	2.45	45	2.19	2.42	45.6	2.19 ¹⁵
2.	Zinc Oxide (Pressed Powder)	1.41	50	2.88	1.42	49.7	2.886 ¹⁴
3.	Asbestos Board	1.77	50	0.94	1.78	50.0	0.94
4.	Industrial Catalyst (CO-conversion ZnO/CuO)	1.92	30	4.50	—	—	—

Results & Discussion

It is quite evident from Table 1, that the thermal conductivity of CuO and ZnO pellets, is in good agreement with the reported data within ± 2 per cent variation, while their bulk density and mean temperature are similar to those of the specimens of a known thermal conductivity. The observed thermal conductivity of a commercial asbestos board when measured at same temperature is also in good agreement with the reported value (Table 1).

Thermal conductivity of an industrial catalyst (CO-conversion CuO/ZnO type) has been found to be 1.92×10^{-3} g. cal sec⁻¹, cm⁻², °C⁻¹, cm. at 30°C. The catalyst consists mostly of ZnO. This value corresponds to ZnO pellet having bulk density of 2.6 g./c.c. (from Fig. 4). But in case of a catalyst specimen the bulk density is 4.5 g./c.c. Again, it has been observed that λ_s of ZnO pellets decreases with increasing bulk density. This value is as low as 1.35×10^{-3} g. cal sec⁻¹, cm⁻², °C⁻¹, cm at 50°C and 3.1 g./c.c. But the λ_s value of all materials increases again after reaching an optimum bulk density. In the case of catalyst sample, the bulk density might

have exceeded the optimum density of ZnO. Further, the presence of CuO to the extent of 20 per cent is also responsible for a higher λ_s value.

It is evident from Fig. 5 that thermal conductivity of all these samples when measured at a particular bulk density increases with rise of temperature. The λ_s vs. temperature curve of the catalyst sample is very much similar to that of ZnO pellet. This indicates that the thermal conductivity of the catalyst pellet is mainly due to its predominant constituent being modified slightly by high pressing and incorporation of minor constituent like CuO.

Acknowledgement

Thanks are due to Dr. B. K. Banerjee, Additional Superintendent, Physical Research Wing, of this Division for his encouragement.

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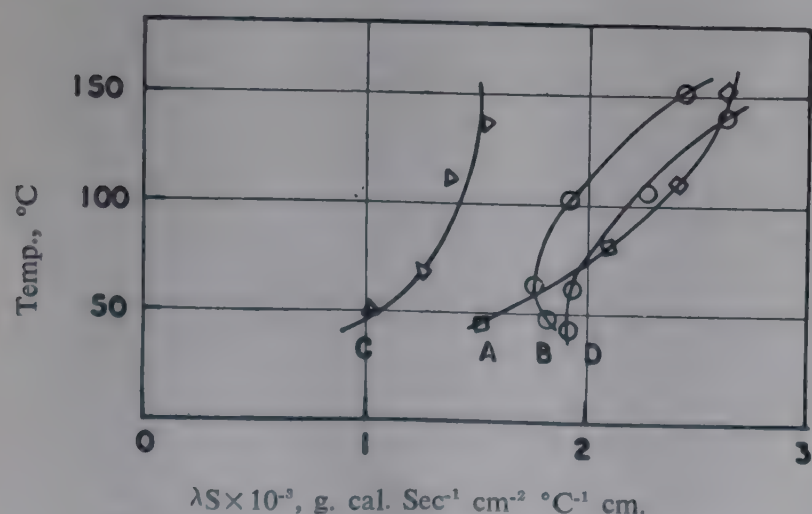


Fig. 5—Effect of Temperature on the Thermal Conductivity of Different Specimens

A—CuO Pellet 3.88 g/cc C—Asbestos Board 0.94 g/cc
B—ZnO Pellet 2.22 g/cc D—Catalyst Sample 4.50 g/cc

A simple "λ" shaped double capillary aspiration system has been devised and with this, atomic absorption spectrophotometric titration has been shown a real possibility. By using this system, interference was removed with the help of a releasing agent without actually mixing it with the sample. Similarly, ionization was controlled with the help of an alkali metal. In addition, the present device can be used, for interference studies, for estimations by addition method and for obtaining multiple standards. The use of this system will save a lot of sample preparations and will economize the use of reagents.

Titration by Atomic Absorption Spectrophotometry Using Double Capillary Aspiration System— A New Approach

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The atomic absorption spectrophotometric titration can be made possible only for the elements which form involatile compounds with interfering ions in stoichiometric ratio and do not dissociate completely in the flame. It is an established fact^{1,2} that by mixing orthophosphate ions with calcium, involatile calcium orthophosphate is formed which depresses the calcium signal. The change in the slope¹ of depression corresponds to 3:2 stoichiometric ratio and then the curve runs flat. The sudden break at the equivalence point can be regarded for titration as the end-point, which can be utilized for estimating the concentration of interfering ions or the interfered elements. Similar end-points have been used for the estimation of calcium³ and lanthanum⁴ by titrating them with phosphate ions using the flame photometric technique. Svehla and Slevin⁴ found that the results suffer from a negative error due to the gradual feeding of the lanthanum solution in the flame thereby decreasing the lanthanum ions. To obtain better results they titrated the sample second time near the end-point, by initially mixing 80 per cent of titrant (phosphate ions) required in the first titration. So far titration in the exact sense is not possible by flame techniques as the test element is being consumed during the observation.

It has been observed⁵ that by aspirating the test element and the depressant into the flame through two separate capillaries no depression occurs. This suggests that intimate mixing of the sample and the depressant

is a necessary criterion for depression to occur, and therefore a necessary condition of titration using flame end-point detection technique, for which solutions should be mixed thoroughly and there should be no change in the concentration of test element during observation.

Present Study

Keeping the above requirement in view, a "λ" shaped double capillary system with a small bulb at the junction has been designed. The sample and the interfering ions were aspirated through the two lower ends of the capillary simultaneously, enabling them to get mixed in and above the bulb before nebulization and at the same time keeping the concentration of the solution constant. Since the solutions are mixed before nebulization, interference occurs unlike in the dual atomization system⁵.

The titration by this technique will not be volumetric as it is not performed by adding small increments of volume of the titrant to a fixed volume of titrate. In this case, a fixed concentration of titrate and increasing concentrations of the titrant (interfering ions) are fed to the flame keeping the rate of aspiration constant. This is unlike the usual photometric titration and the one used by authors^{3,4} employing flame photometric technique for end point detection.

In the present investigation, preliminary studies on interference effect and titration of phosphate ions with respect to calcium have been carried out with the above capillary system. Besides these, other applications of this capillary are also discussed in this paper.

Experimental

A Perkin Elmer model 303 atomic absorption spectrophotometer and calcium and strontium hollow cathode lamps of the same make were used. The analytical conditions were kept same as suggested in analytical methods⁶. For the ionization suppression study, strontium ionic line 4077 Å was used.

Double Capillary System: A hypodermic needle (No. 22) was taken and was cut at a length of 0.5 in. from its base. A push-fit perspex socket with two small holes was made such that when it was pushed to the base of the needle, a small space was left which acted as a bulb for mixing the solutions. Two polythene capillary tubes, 5 in. long having o.d. and i.d. 0.43 and 0.05 in. respectively, were inserted through the holes of the socket and fixed with an adhesive. The needle end was connected to the nebulizer with the help of 1 in. of above polythene tube. The shape of the system was like a "λ".

Standardization of Double Capillary System: A 20 ppm calcium solution was aspirated through one of the lower ends of the system and de-ionized water through the other and *vice versa*. That the absorption in both the cases was made equal by adjusting the length of the lower ends.

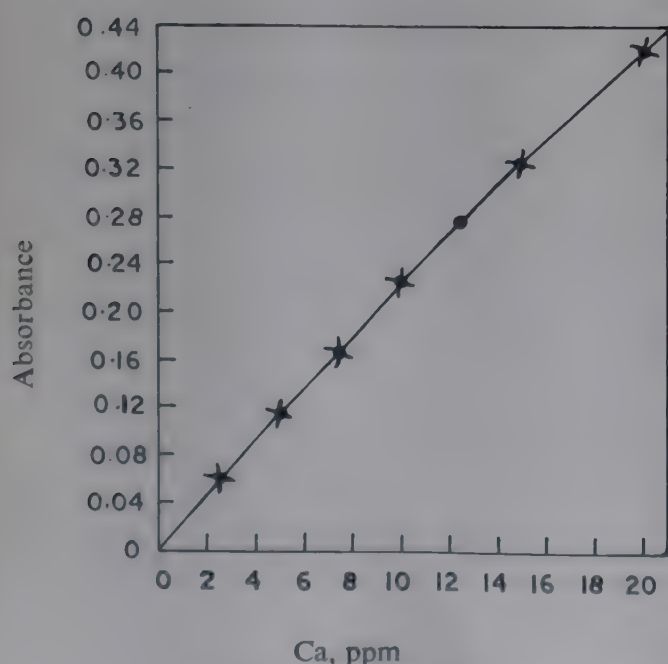


Fig. 1—Calibration Curve for Calcium
× Standards
● Additive Standards

To confirm that absorbance due to solutions aspirated through the two capillaries was additive, a 5 ppm calcium solution was continuously aspirated through one end and water and calcium standards from 2.5 to 15 ppm through the other. It is found that the absorbances are additive and these additive values fall exactly on the simple calibration curve (Fig. 1) plotted from the points obtained by aspirating water through one end and calcium standards through the other. This obviously suggests that by using the above system, multiple standards can be obtained with the help of a few made ones. Also the standard addition method can be used without actually making the addition standards.

Interference of Phosphorus on Calcium: A 20 ppm calcium solution was aspirated through one end and water and phosphorus standards (made from ammonium hydrogen phosphate) through the other. The sudden break in the interference curve (Fig. 2) corresponds to the 2:1 concentration ratio of calcium to phosphorus. This curve can be used for estimation of phosphorus as was done earlier^{7,8} in this laboratory. The advantage of the double capillary system is that a fixed amount of calcium is not to be added to the standards and the samples. The effect of certain substances on a test element can be studied simply by aspirating them simultaneously through the lower ends.

Titration: As mentioned earlier, Svehla and Slevin⁴ obtained negative error during their flame photometric titration. Further, the addition of the titrant, its shaking and then aspirating into the flame is very inconvenient. It is also felt that the dilution of the sample due to gradual addition of the titrant to it will cause some decrease in signal intensity even after the end-point is reached, hence a sharp end-point is not expected. This may cause error in accurate detection of the end-point. By using the present capillary system, these drawbacks are removed.

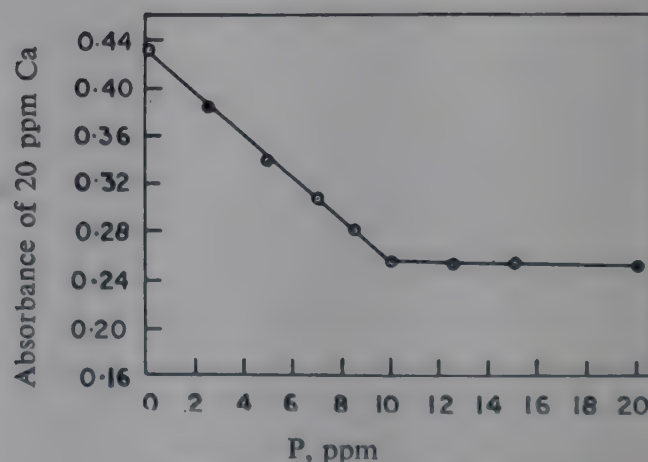


Fig. 2—Phosphorus Interference Curve

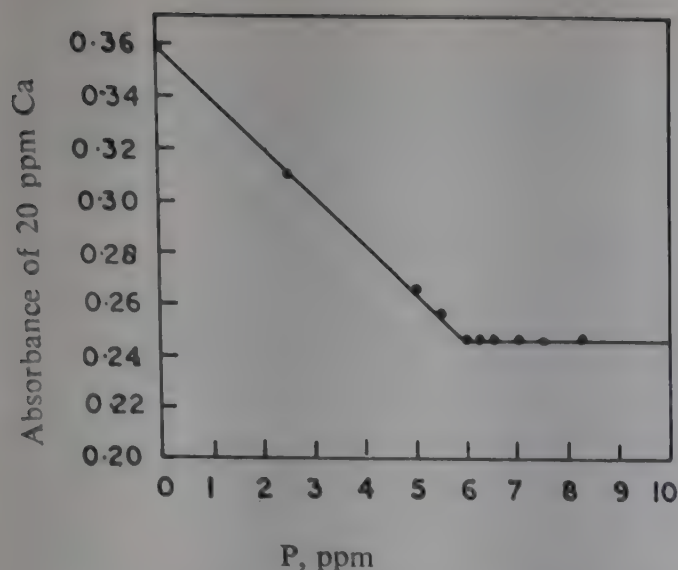


Fig. 3—Estimation of Phosphorus by End-point

The break in Fig. 2 can be utilized for estimation of calcium by titrating it with phosphate ions. In the present work, instead of calcium, phosphorus is determined using the same end-point. A solution containing 20 ppm calcium and 4 ppm phosphorus (added) was aspirated through one end of the capillary system and water as well as phosphorus standards through the other end. The values are plotted in Fig. 3. It is seen that the end-point comes at 6 ppm. of phosphorus instead of at 10 ppm (calcium in the solution being 20 ppm) suggesting that the sample contained 4 ppm phosphorus initially. This is same as the phosphorus added in the solution.

The addition method used by Sanyal et al⁹ for phosphorus determination by flame photometry can also be used in the present case, without making the addition standards. A blank (20 ppm Ca) was aspirated through one end and water through the other. Using the blank value, phosphorus was estimated by extrapolation of Fig. 4, which was obtained by plotting the values of the unknown sample and two phosphorus standards, obtained in the above case.

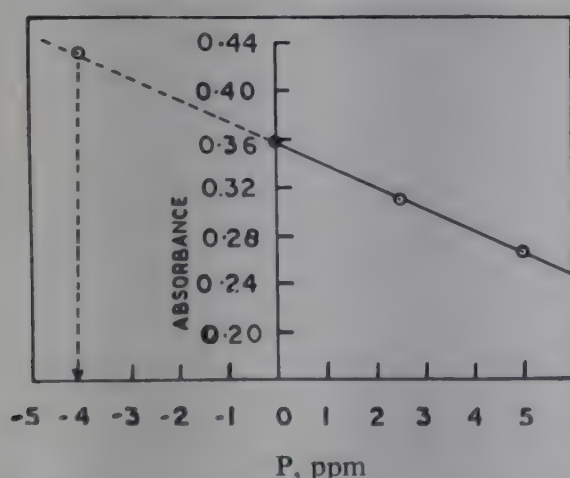


Fig. 4—Addition Curve for Phosphorus Estimation

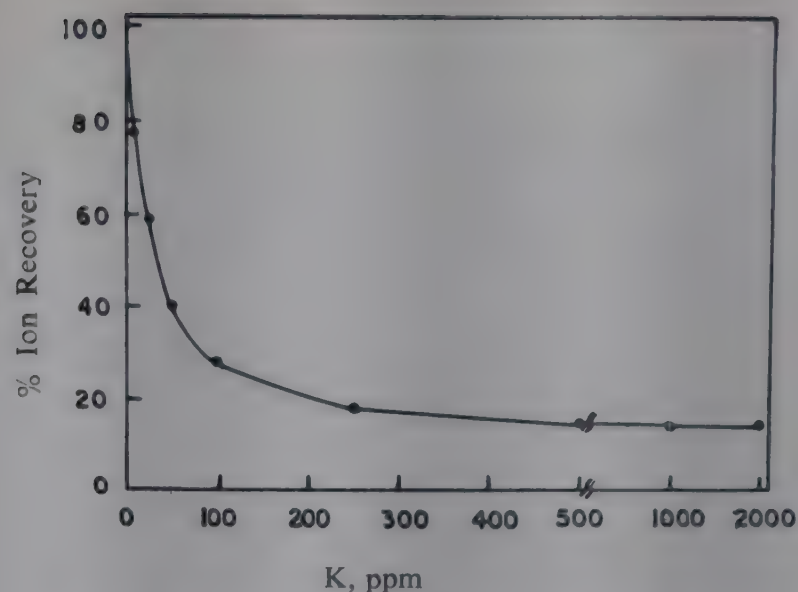


Fig. 5—Suppression of Ionization of 100 ppm Strontium by Potassium

Releasing Action: A study on releasing the strontium (30 ppm) from phosphorus and aluminium (200 ppm each) was carried out by aspirating these solutions through one end of the capillary and a 2 per cent lanthanum (as lanthanum chloride) solution through the other. It was found that the interference was completely eliminated as in case of usual single capillary system. The present device will be of much use in the analysis where interference is to be removed. It saves a lot of sample preparation and economises the use of reagents. Further work in this line is in progress.

Suppression of Ionization: In high temperature nitrous oxide-acetylene flame, a number of elements suffer from ionization interference, which is significant in case of alkali metals and strontium even in air-acetylene flame. To eliminate this effect, a salt of easily ionizable atoms like sodium or potassium is added in the samples and standards. To avoid sample preparation, the salt solution can be aspirated through one end continuously and the samples as well as standards through the other. The suppression of ionization in case of 100 ppm strontium was studied using the ionic line and by aspirating potassium solution through one end of the capillary. It is evident from Fig. 5 that the ionization is inhibited.

Conclusion

The double capillary system used for the aspiration is convenient for estimating phosphorus and similar interfering ions using indirect method. The exact end-point for titration can be found out without the negative error as obtained by earlier workers⁴. The other advantage during titration is that the sample does not get diluted, therefore, the error in the end-point detection due to dilution is avoided. In addition to the above, this capillary can be usefully employed for the following general

purposes. (1) Estimation by standard addition method; (2) making of multiple standards from the few made ones; (3) to study the effect of interfering ions and other substances on the absorption of test element without actual mixing; (4) elimination of interference without mixing a releasing agent; and (5) suppression of ionization without mixing the alkali salts.

By using the double capillary a lot of sample preparation and the wastage of reagents are eliminated. These advantages can be equally applicable to the flame photometric and atomic fluorescence spectrophotometric studies. This capillary can be employed without disturbing the nebulization arrangement incorporated in the commercial equipments and shows promise for its use in the analyses based on flame technique. Further work on its use is in progress.

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Stainless steel strips used for fixing the asbestos diaphragms to the cell frames in the electrolysis plant at Nangal developed cracks between the positions of the fixing bolts. The cracks have been found to be of the intercrystalline type and have been ascribed to stress corrosion of stainless steel in 25 per cent caustic potash at 80°C.

Intercrystalline Corrosion of Stainless Steel in an Alkaline Medium: A Case History

By K. M. VERMA, M. P. GUPTA, B. R. CHAKRABARTI & A. K. ROY,
*Planning & Development Division,
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At Nangal*, hydrogen for ammonia synthesis is obtained by an electrolytic process. Each electrolyser consists of a battery of 108 bipolar cells clamped together tightly so as to form a filter press-type apparatus. Electrodes are mounted in pairs, each pair being separated and divided by a central metallic plate. The electrodes facing each other are separated by a double diaphragm of pure asbestos, which is used to ensure the production of highly pure gases. These diaphragms are fixed to the cell frame by strips clamped with screws. Originally, the strips were made of nickel-plated carbon

steel, but during use, nickel plating was found to come off so that the mild steel strips were getting corroded. For this reason, the strips were later changed to those made of 18:8 Cr-Ni stainless steel. On inspection recently some of the strips were found to develop cracks. These strips are exposed to the action of 20-25 per cent caustic potash at about 80°C.

Tests and Observations

Visual Observation: Visual examination of the strips from both hydrogen and oxygen sides revealed some cracks midway between the position of the fixing bolts.

*FCI Ltd., Nangal Unit, Punjab

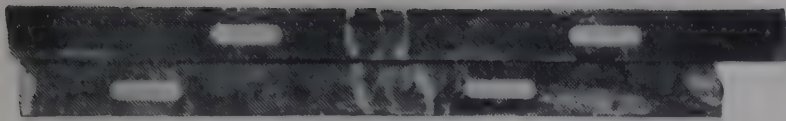


Fig. 1—Cracked Strips

On removal of the asbestos material and black deposits adhering to the strips, it was observed that the strips had developed fine cracks and the direction in all the cases was along the breadth (Fig. 1).

Chemical Analysis: Chemical analysis revealed the material to be the AISI 304 stainless steel. Its tensile strength and hardness values were as under:

TABLE 1—ANALYTICAL CONDITIONS

Sample	U.T.S., lb/sq. in	Hardness, BHN
New unused strip	43.4	158
Used hydrogen side strip	24.3	158
Used oxygen side strip	22.3	158

Metallographic Examination: Several samples from the affected and unaffected portions of the used strips as well as some from the new ones were subjected to metallographic examination. All of them showed the normal austenitic structure with presence of slip bands. The used strips showed numerous intergranular cracks about midway between the positions of the fixing bolts irrespective of gaseous environment (Figs. 2-5). Fig. 2

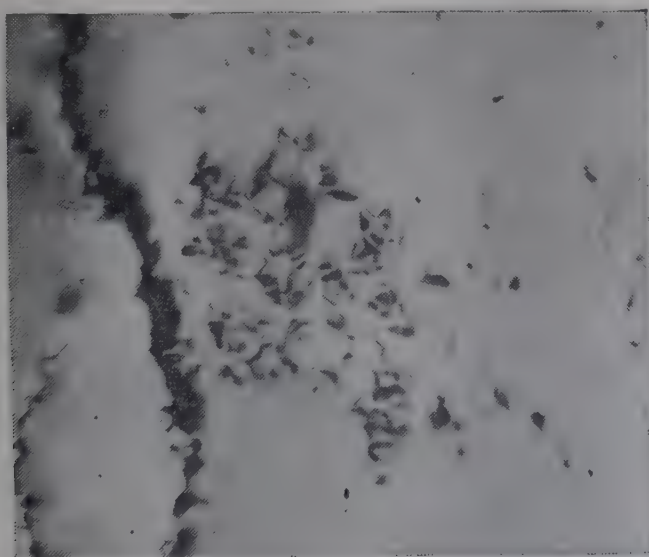


Fig. 2—Photomicrograph of the Failed Strip in the Unetched Condition showing Numerous Long-Cracks and Honey-comb type Cracking Pattern (X 115)

is a micrograph of the hydrogen side strip adjacent to a visible crack in the unetched condition showing numerous long cracks and honeycomb-type cracking pattern indicative of the attack on the austenitic grain boundaries. Figs. 3 to 5 indicate the same intergranular cracking pattern.

Discussion

Chemical analysis and metallographic structure do not indicate any defect in the material but there is evidence of severe stress in the material as indicated by the presence of slip bands. The photomicrographs clearly indicate severe intergranular attack. The reduced tensile values of the used strips are naturally due to the incipient cracks existing in the material. The intergranular failure could be ascribed to stress-corrosion failure of stainless steel due to conjoint action of 25 per

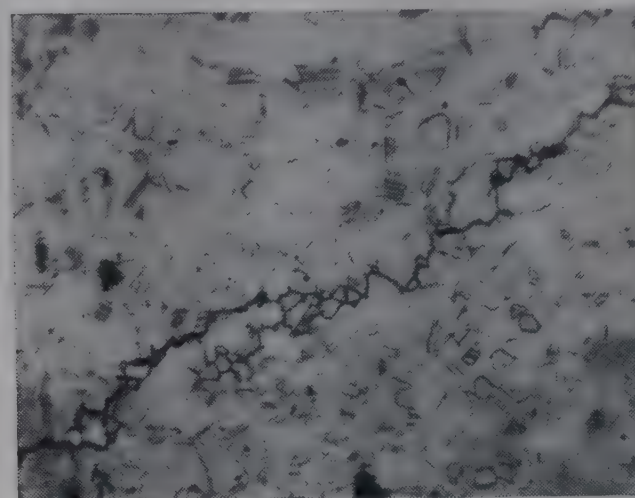


Fig. 3—Photomicrograph of the Failed Strip showing Austenitic Grains with Presence of Slip Bands and Cracking Pattern of Intergranular Type. (X 115)

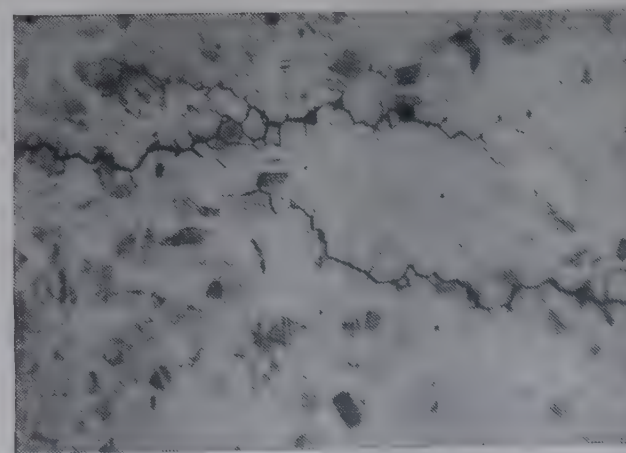


Fig. 4—Photomicrograph of the Failed Strip showing Austenitic Grain with Presence of Slip Bands and Cracking Pattern of the Intergranular Type. (X 115)

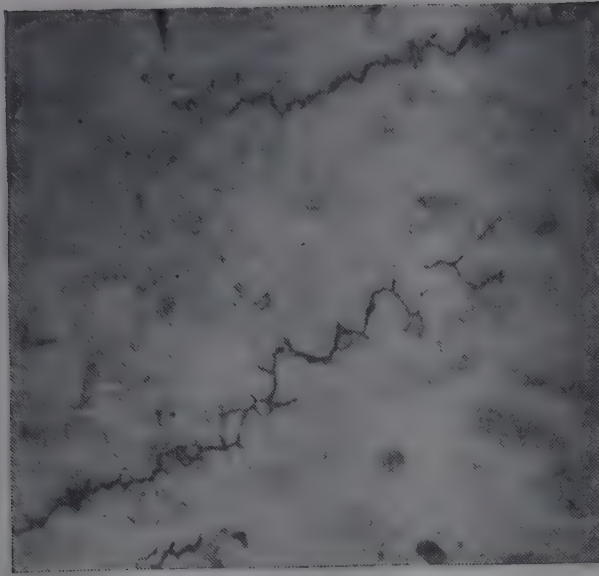


Fig. 5—Photomicrograph of the Failed Strip showing Austenitic Grains with Presence of Slip Bands and Cracking Pattern of Intergranular Type. (X 115)

cent caustic potash at 80°C and stress incorporated in the material during fabrication. The presence of hydrogen and oxygen might not be affecting the failure in any way. The conditions have most likely been aggravated due to the crevice conditions arising out of the fact that one side of the strip was in close contact with the diaphragm while the other was exposed to the cell chamber.

Wanklyn and Jones¹ have clearly established the intercrystalline failure of stainless steel in an alkaline medium under crevice conditions and showed that even stabilized stainless steel may suffer from this type of attack.

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Technical Digests & Abstracts

Evaluation of Wet Processes of Phosphoric Acid

In India most of the processing of rock phosphate, mainly because of utilization of its lower grades, is attributed to the manufacture of phosphoric acid, which in turn is converted largely to calcium and ammonium phosphates for concentrated fertilizers at the production site. Of the processes for phosphoric acid, wet process is most common using either sulphuric or hydrochloric acid. The sulphuric acid method yields an important by-product, viz. calcium sulphate produced in different crystalline forms, which influences the filtration of the gypsum-phosphoric acid slurry. The basic commercial processes produce the following types of crystals of calcium sulphate: (i) dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) (ii) hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), (iii) primarily hemihydrate but subsequently changed to dihydrate, (iv) precipitate as dihydrate but converted to hemihydrate.

In a paper* presented at the conference on the Design and Analysis of Chemical Process Synthesis held during Oct. 27-28, 1969 at the Indian Institute of Technology, Kanpur, Sri B. B. Roy, Asstt. Chief Engineer, P & D Division, has discussed the design and techniques of the reactors, merits and demerits of various types of modern filtration and other aspects viz., concentration of the acid and choice of materials of construction of different equipments used. He has also discussed the various possibilities of utilization of the by-product.

Process Technology: Rock phosphate is usually ground to a fineness of about 90 per cent through 100 mesh (B.S.S.) and premixed with recycled weak phosphoric acid, the object of premixing being to (i) prevent direct contact of unreacted rock with sulphuric acid which may form a coating of insoluble calcium sulphate over rock phosphate and (ii) keep Ca^{2+} and SO_4^{2-} concentration low and homogeneous in the slurry so as to get controlled crystallization of calcium sulphate. In the slurry, the liquid phase is mainly calcium sulphate with small amounts of unreacted rock. Calcium sulphate first develops supersaturation, which later results in crystallization. Normally 6-8 hours are sufficient for conversion upto 99 per cent, although the time required for higher operating temperatures is much lower.

*Evaluation of Various Wet Processes Phosphoric Acid facturing Techniques.

Various processes developed so far are divided into the following categories: (i) those yielding acid of high strength, (ii) others yielding of normal strength. In the former the crystals are precipitated out in the form of anhydrite and hemihydrate crystals. Studies at TVA have shown that a stable, rapidly filtering anhydrite could be formed at 110°C . When the acid concentration is sufficiently high (40-45 per cent P_2O_5), the proper temperature and acid concentration to give a stable anhydrite crystals are given by the expression $2P+t=186$, where P is the concentration in P_2O_5 of the acid and t temperature.

In the hemihydrate process also high temperature is used for speeding the reactions and reduce the viscosity of phosphoric acid, so that the acid filters rapidly, especially where higher concentration is obtained. Stable hemihydrate crystals can be grown over a wide range of P_2O_5 concentration. The factors affecting the performance of this process are relative reactor volumes, control of precipitation and temperature (85 to 110°C) and proper mixing but the disadvantages are corrosion, for which costly material of construction is required, and blinding of the filter cloth due to hydration. Fisons have developed a process capable of producing directly 50 per cent P_2O_5 acid, which is based on separating hemihydrate by a single filtration step; there is no danger of formation of gypsum either in the reaction system or on the filters and of calcium sulphate scale. TVA have succeeded in producing metastable hemihydrate agglomerates by a foaming process of distributing sulphuric acid in the reactor.

The conventional dihydrate process, which is most widely used, yields normal strength acid. The reactor comprises a series of agitated compartments maintained around 70-75 per cent and sulphuric acid is fed in the second one; the slurry is cooled either by vacuum evaporation or air injection either on the surface or inside. This Division of FCI Ltd., has also developed a dihydrate process based on multi-tank system, where P_2O_5 recovery efficiency is around 96 per cent.

Reactor Design: As regards the reactor, the following are some of the key points for consideration: (i) proper shape or size of the equipment to ensure good distribution and mixing, etc.; (ii) proper choice and design of the agitator to provide sufficient intensity of agitation;

(iii) proper recirculation and recycling of reactants and products; (iv) temperature control by slurry cooling to remove excess heat of reaction and acid dilution, thus controlling the super-saturation; and (v) control of the rate of solid and liquid feeds. The earlier reactors, viz. of Dorrco, Chemico, Nissan, NKK, etc., were separate cylindrical tanks in series, while Prayon design was multi-compartment type large tanks.

The single tank system provided with interval partitions has come up rather recently. Its integral construction is economic and provides better internal recirculation thus avoiding an external pump for recirculation. In the designs of St. Gobain and UCB, there are no baffles inside but the agitators are designed to give a horizontal or vertical motion to the slurry. Subsequently, Dorr-Oliver, Chemico, etc. also developed a single-tank system provided with internal baffles and an internal concentric surge tank (in the case of Dorr-Oliver only) for stabilizing the filter-feed slurry.

In the multi-tank system, e.g. Prayon, normally two cylinder tanks with radiation partition walls in each are provided, thus providing 8 compartments. Fisons use a cylindrical vessel containing 3 or more compartments, while Singmaster and Breyer's hemihydrate reactor comprises a premixer followed by secondly digester vessels; Nissan uses a series of cylindrical vessels, the first one called premixer, the following one or two for hemihydrate formation and the last ones for hydration and crystallization. In the Prayon dihydrate-hemihydrate process, a single rectangular compartmental vessel is used in both di- and hemihydrate sections.

Thus, the type, number and arrangement of the units also showed marked variations in the design. In the dihydrate process, the single tank reactor seems to be more compact and cheaper compared to multi-tank system, though there are chances of short-circuiting of reactants and less operation flexibility. The agitators in general are of propeller and turbine types and high speed is not desirable. The pumps are vertical, centrifugal or vertical submerged centrifugal types, the latter type being preferred because of their low maintenance and relatively trouble-free operation. In most of the modern designs, submerged pumps are used but they are costlier.

The reactor temperature control is normally carried out by air or vacuum cooling of the recirculatory slurry, the former being expensive for incorporating scrubbers. In vacuum cooling the requisite quantity of slurry is circulated through vacuum flash chambers, where it is cooled due to evaporation and the cooled

slurry is recirculated in the reactor whereby temperature is controlled.

Filtration: The present types of filters are the horizontal moving belt, rotary table and, the latest and most effective, the horizontal tilting pan. The use of moving belt type is confined to small plants and except a few old installation there are no new plants going in for this type. The horizontal table filter, which appeared sometime after 1945, has a series of sector-shaped filter pads mounted on a rotating table about a central automative valve connecting each sector in turn to vacuum receivers for various washes and removals. In a recent improvement of the table filter, a continuous rubber belt forms an edge to the cake, thus improving washing near the cake edge, and which can be drawn away for effective cake removal and cloth washing. It has several advantages over the tilting pan type, whose construction is very complicated and also costly.

Concentration: The physical properties of the wet process phosphoric acid boiling point elevation at higher concentration and dissolved impurities are the major factors influencing the design of suitable evaporators. Single-effect evaporation of forced circulation type is the current practice. Normally, about 75 mm. of mercury absolute pressure is maintained which can maintain a boiling temperature not exceeding 85°C. Submerged combustion technique is also sometimes adopted.

Corrosion: Corrosion is due to high temperature, presence of halogen acids and abrasive solids. Originally, hard rubber-lined steel was used but now-a-days many designers are using 3-part laminations consisting of a soft layer bonded to the steel to take care of expansion, a hard inner layer to prevent acid penetration and a final inner lining with soft rubber to withstand erosion. Vessels, like digestion tanks, reactors and evaporators usually have a lining of carbon bricks over the rubber in order to protect the latter. In a high temperature operation (100°C) in a hemihydrate process, a carbon brick lining over rubber lining is essential.

If a chloride-free rock having sufficient silica is the feedstock, AISI 316 L.C. stainless steel is good enough for filtration to avoid the formation of hydrofluoric acid; more recently, AISI 317 has been preferred. Where chlorine is present, a special stainless steel HV9 is used. For the filter cloth, polypropylene mono- or multifilament is used. For pumps and agitators which are subjected to severe abrasive conditions, alloy 20 is extensively used as a material of construction; but in presence of chlorides HV9A or Uranus B-6 is a good choice.

Utilization of By-product: In India, all the operating plants follow dihydrate process and the by-product gypsum is used in ammonium sulphate production except in the Vizag plant where it is thrown away. The other uses of gypsum are: production of wall-board, as retarder of cement and production of sulphuric acid and cement.

If the economics of a cement-sulphuric acid process is ultimately proved attractive, the most important problem will be the selection of the proper process technique for economic production of phosphoric acid, at the same time getting by-product gypsum in a relatively pure form, especially with regard to P_2O_5 and fluorine. No dihydrate process can possibly meet this demand.

Recently Fertilizer Corporation of India have awarded a contract for installing a 360 te P_2O_5 /day phosphoric acid plant at Sindri for the Prayon process to M/s FACT, who are the licensee of Prayon. The by-product gypsum will be utilized for ammonium sulphate production and the chalk will be utilized for cement production locally by the Associated Cement Co. A dihydrate/hemihydrate process has been selected, which though involving considerably higher investment than in the conventional dihydrate plant will produce a suitable quality acid.

ABSTRACTS

*The Application of Gas Chromatographic Techniques to the Analysis of Complex Hydrocarbon Mixtures Derived from Coal and Petroleum** by N. C. Saha and G. D. Mitra (P & D Division, FCI Ltd.): Gas chromatography is undoubtedly the best technique today for the analysis of hydrocarbons in any complex mixture. A complex sample should be divided into three stages, viz. fractionation, fine separation and peak identification. Various GC-techniques have been discussed for the fractionation of hydrocarbons according to boiling point, carbon

number, retention index and structural types. The aim and choice of column technology and mode of operation should be such as to permit maximum possible resolution of all the components in separate chromatograms for different classes of hydrocarbons, such as, normal alkyl, and cyclo paraffins, olefins and aromatics. Application of the latest extensions of Kovats' retention index, particularly, its variation with column temperature will give positive identification of peaks and shoulders from such chromatograms to the extent of availability of data from literature or from authentic samples. Beyond this, help should be taken from the recently developed combination of GC with structure specific detectors, like mass spectrometer. Some of the principles mentioned in this investigation have been illustrated with gas chromatograms obtained in this laboratory with packed as well as capillary columns. Since the methods of production and utilization of hydrocarbons often demand rapid analysis of the changes on structural types or composition of a particular fraction, the detailed schemes of analysis discussed in this study can easily be shortened and modified.

A New Process for the Preparation of Water-Soluble Phosphatic Fertilizer from Iron-Rich Phosphatic Rocks† by H. Roy, S. K. Adhya and S. K. Sharma (P & D Division, FCI Ltd.): A process has been developed for the preparation of a water-soluble phosphatic fertilizer from low grade iron-rich phosphatic rocks. First of all ferro-phosphorus is prepared by heating these rocks with additives, like mica and limestone, at 1300°C. The phosphorus of these rocks is concentrated in the form of ferro-phosphorus to the extent of 56.5 per cent (as P_2O_5). It is then digested with hydrochloric and nitric acids when a solution containing a mixture of phosphoric acid and ferric chloride is formed. It is extracted with diethyl ether and iron salt is completely removed from phosphoric acid. On neutralizing the resultant solution with ammonia, a water-soluble N-P fertilizer, comprising mostly of diammonium hydrogen phosphate, is obtained.

*Paper communicated to the Symposium on Chemicals and Oils from Coal held at the Central Fuel Research Institute (CSIR), Dhanbad, in December 6-8, 1969.

†A full paper will be published in *Technology* in due course.

Reviews

Seminar on Fertilizer Marketing 1968—Proceedings, The Fertilizer Association of India, New Delhi

The seminar on Fertilizer Marketing sponsored by the Fertilizer Association of India held in New Delhi in December 1968 discussed various aspects of marketing of fertilizers in India in the present and future contexts. 63 papers were altogether read by eminent persons connected with this industry on the establishment and operation of effective and efficient marketing sales promotion and logistics of fertilizer distribution. At present the fertilizer consumption in India per acre is one of the lowest in the world. The planners feel that the consumption of fertilizers at the end of Fourth Five Year Plan would be N: 3.73 million tonnes, P_2O_5 : 1.74 million tonnes and K_2O : 1.11 million tonnes and at the end of 1980-81 N: 8 million tonnes, P_2O_5 : 4 million tonnes and K_2O : 2.5 million tonnes compared to the present total consumption of all fertilizers of only 1.5 million tonnes. Whatever be the targets there is no doubt that during the next decade the indigenous production of fertilizers is bound to increase to several times of that at present and increase in fertilizer consumption in India would be very large to meet up the future targeted agricultural production in the country. The papers read in the seminar give valuable suggestion regarding the techniques of sales promotion programs and efficient marketing machinery to enthuse the unsophisticated and simple farmers for adopting new techniques of cultivation with chemical fertilizers. The imported fertilizers are distributed through the state governments. In a situation of shortages it is the responsibility of the government to impose certain controls in order to ensure that the scarcity of fertilizers is not exploited by some distributors indulging in malpractices. To encourage private investment in setting up new fertilizer plants in the country the Government has liberalized policy allowing the fertilizer manufacturers to market their products through their distributors and determine their prices. This marketing relaxation was also extended to existing factories from 1st Oct., 1968 subject to government's option of 30 per cent in the case of straight nitrogenous fertilizers. Factories are always free to market their complex fertilizers as they pleased. But the state governments would have to ensure that the agency of distribution appointed by fertilizer manufacturers appreciate the needs of fertilizers of the farmers.

Fertilizer shortages are expected to be over and changes in the market resulting in its transformation from a seller's market to a buyer's one are taking place. The twin objectives of fertilizer marketing are maximum consumer satisfaction and profit to the business. But the fertilizer price in India is very high compared to other countries of the world.

To popularise the use of fertilizers among the farmers whose purchasing capacity is very low, the prime objective of the marketing should be to supply to them fertilizers at fair price so that they have adequate incentive to use them. The Government should give more assistance to the cultivators in the form of subsidies and price reductions of fertilizers. Availability of fertilizers nearest to farmer's home and supply to them in time are crucial in promoting fertilizer sales. The scope of the marketing system has to be enlarged to introduce balanced fertilization and combination of nutrients to suit different soils and crops. Extensive soil tests should be carried out throughout the country as a prerequisite to scientific application of fertilizers. Pesticides and herbicides might also be supplied along with the fertilizers to farmers. They should also be given by the manufacturers proper technical training regarding the application of correct dosage of fertilizers for maximum return of agricultural yield. This is possible through vigorous publicity regarding the uses of fertilizers and their advantages through film shows, meetings, exhibitions and practical demonstrations. For efficient marketing the manufacturers have also to pay due attention to the transportation, storage and packaging of fertilizers so that they are not spoiled.

Recognising the general awareness of the need for establishing an efficient and effective marketing organisation, the Seminar recommends that the organisation should be so structured as to perform the following functions:

- (1) Making the fertilizer available to the farmers;
- (2) Arranging necessary credit to dealers and farmers;
- (3) Developing and expanding the market for promoting the efficient use of fertilizers and complementary inputs;
- (4) Providing technical and professional service.

The marketing organisation should constantly aim at improving the efficient use of fertilizer and other inputs.

[Benoy K. Banerjee]

Fertilizer Industry Round Table* 1968

The 18th Annual Meeting of Fertilizer Industry Round Table presided over by Dr. Vincent Sauchelli was attended by the experts in the fertilizer industry. Such professional body meeting is always a good forum for exchange of views by the people rich in their experiences. The proceeding of such meetings is a useful document as is evident from this proceeding which is nicely edited and printed and contains slides, tables, graphs and other illustrating material. The papers presented covered the many aspects of fertilizer industry right from day to day working to new innovations. The opening paper was on nitrophosphate and then more papers on this subject followed in third session. In the first session there was a panel discussion on materials of construction for fertilizer plant which covered with other things advents of new corrosion resisting alloys, uses of plastic material in plants. The second session touched the subjects like bulk-blending equipments, storage, handling etc. The third session started with the first two papers devoted to micronutrients. And then came the ticklish subject nitrophosphate which was discussed in good length. All the papers described the chemistry, process and economics of the nitrophosphate but conspicuously no paper referred to efficacy of agronomic value which is still in doldrums, except some passing remarks. The meeting ended with the last two papers devoted to polyphosphates.

Materials of Construction for Fertilizer Industry

In the first session there was a panel discussion on materials of construction for fertilizer industry, Dr. Enrico Pellitti as its panel leader. Mr. E. A. Tice talked about some brand new alloys which are available both as castings and as wrought materials. Illium P, and CD-4MCU alloys, both somewhat similar having greater hardness, better erosion resistance, are high chromium alloys, with some nickel molybdenum and copper additions, which improve acid corrosion resistance. Another alloy Illium-98 has been especially designed for the handling of hot sulfuric acid solutions, particularly in the higher concentration ranges. These new cast materials are finding their place in pumps, valves and other components of this type. Inconel 625 and Hastelloy G, (nickel base with about 20 to 22 per cent chromium and considerable molybdenum additions) are starting to come into play in phosphoric acid production. Mecha-

nical properties of these alloys are similar to those of stainless steel, with a little higher strength. They can be welded with companion electrodes and have excellent ductility. There are two new alloys available, one a wrought material of 50 Cr and 50 Ni, and one a cast material only of 60 Cr and 40 Ni which provide unusually good corrosion resistance for extremely high temperature sulfur conditions, either sulfur dioxide or hydrogen sulfide.

Mr. W. E. Rushton spoke about materials of construction for phosphoric acid evaporator. He said that present rubber linings are limited to temperatures below 200°F. Due to the high boiling point elevation of phosphoric acid, this limitation restricts all evaporators to single effect units, and vapor heads must be made very large to allow for very low pressure operation. Materials suitable for higher temperatures would allow the use of multiple effect evaporators, with resultant savings in steam and water consumption. If the cost of the material was no higher than for rubber-lined steel, the overall cost of the evaporator installation could be reduced. Another severe limitation of rubber, said Mr. Rushton, is the difficulty of making repairs. New rubber used for patching must be vulcanized with steam for periods of 48 to 60 hours. This is very time consuming and costly. An additional disadvantage is that after several years of service, it is often very difficult to obtain a satisfactory bond between the old rubber and a new patch. Satisfactory experience with Alloy 20, another material of construction, is limited to acids produced from Florida and Western rocks. Any other rock source must be carefully reviewed, and in many cases may require more expensive alloys. For instance, acids produced from some African rocks may contain a fair amount of chlorides. With this condition a French alloy, Uranus B6, or Hastelloy "C" must be used. The wrought form of Alloy 20, used to fabricate the lump screen, seems to be less susceptible to corrosion than the castings in the pump. However, velocity across the screen is generally fairly low, and the erosive action of the CaSO_4 crystals tend to keep the screen clean so that conditions less likely to cause corrosion are maintained. A new alloy, Neonel could not give satisfactory performance, so Neonel exchangers were replaced by graphite exchangers.

Though there are several satisfactory lining materials for urea reactors, several factors are to be considered relative to their selection. Some of the important ones are: process to be used, pressure vessel fabrication technique, availability of manufacturing and repair facilities. G. R. James stated that the data collected so far indicate that results of tests with corrosion spools in urea reactors can be frequently contradictory and sometimes mislead-

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ing. And that generalizations cannot be made except on the basis of actual plant experience.

The use of plastics in the manufacture of fertilizers shows numerous advantages: corrosion resistance, lightness, non-sticking properties, ease of fabrication, easy repairing of thermoplastic and polyester equipment, relatively low cost. Mr. P. Moraillon explained how some plastic materials are finding application in various fertilizer plants. The most economical material is usually plain PVC, which should be used wherever the temperature allows it, either the normal impact type, or the high impact type. With higher temperatures, one has a choice between PVC hooped by fiberglass-reinforced polyester, PVC with internal metallic reinforcement, polypropylene, and reinforced polyester. Polypropylene units, especially pipes, are usually more economical than reinforced PVC units, on account of the rather high cost of the reinforcement operation. Process piping and equipment made out of PVC hooped by reinforced polyester are usually cheaper than the same entirely made out of fiberglass-reinforced polyester. In the first case, the resin used is cheaper, since a high chemical resistance is not necessary. On the contrary, polyester is presently the first choice every time a high mechanical resistance is required, particularly at temperatures over 80°C. Reinforced polyester may also be used as a lining. In both forms, reinforced polyester will be likely to replace more and more rubber coatings, may be even anti-acid brick linings. If we take into account the phenomenal growth of this material in the past few years, the speaker guessed that it will not be long before phosphoric acid reactors of big capacity are made out of reinforced polyester.

Mr. R. C. Berry narrated some case histories of materials of construction and plant operators. He drew the point at home that by trial and error method one can decide the suitability of the plant material. Moreover, evaluation of materials of construction for an integrated system should be extended to all of its components rather than limited to some sections of it, and related to actual service to which the system will be subjected. He stressed both supplier and user should analyse the material.

The panel discussion ended with a talk on developments in "Attack Tank Lining" by Mr. K. Harrison. He said that carbon bricks set in a well formulated furnace phenolic resin cement, with pure carbon fillers, are in common use and do provide excellent service life. Carbon bricks with very low ash content 7 per cent will resist the fluorides present in the slurry with no evidence of deterioration, with the added advantage of improved

resistance to abrasion. Earlier practice for concrete vessels was to use hot applied asphalt, about 1/4" thick; it is still specified today for some applications. The alternative was a sheet material, manufactured from petroleum tar and reclaimed rubber. Both materials have been fairly successful, but have the disadvantage of being difficult to apply, which makes them quite expensive in terms of labour. This is particularly true with hot applied asphalts, because of the difficulty of building up the required thickness on large vertical surfaces. To give body and strength to the membrane, layers of fiberglass mesh were introduced. In wet process phosphoric acid attack tanks, this method is not recommended, because if any part of the fiberglass is exposed or insufficiently covered with the asphalt it will be attacked by the fluorides. Natural gum rubber is an ideal membrane material for attack tanks because of its excellent resistance to the acids present in the reaction. Application and vulcanization of rubber in sheet form to large concrete surfaces, however, is extremely difficult, and the costs are prohibitive. The system is essentially an underlay coat, based on natural rubber latex mortar 1/8" thick, followed by the sprayed natural rubber also 1/8" thick. It can be (and often is) applied to "green" concrete. Can monolithic linings be a substitute for rubber membrane or carbon brick system as latter involves more costs? The author concluded that apart from the technical problems which have yet to be solved, monolithic linings are not yet a substitute for the conventional membrane and brick sheathing system on the basis of cost.

Bulk-blending Equipment

Bulk blending of fertilizers has grown to be a major segment of the industry. In bulk-blending obtaining good mixing at the point of production and prevention of segregation of the fertilizer components in the subsequent handling are problems. The second session started with a talk by G. L. Bridger on mixing efficiency of fertilizer bulk-blending equipment. Study was carried out to determine the ability of several types of mixers being used in commercial operations to produce a homogeneous bulk blend fertilizer. The fertilizers used were ammonium nitrate, high analysis superphosphate and potassium chloride. Tests were made on the efficiency of mixing of fertilizers in six bulk-blending plants and on one pilot plant scale mixer. The plant scale mixers tested were a cylindrical rotary mixer, a concrete mixer, a ribbon mixer, a vertical tower mixer, a cone mixer, and a screw mixer. The pilot plant mixer tested was a Munson rotary mixer. Mixing efficiency was judged by deviation from average analysis of a series of samples

taken during discharge of the mixer. Best mixing was achieved by the screw conveyor mixer, which is a continuous mixing unit, but proportioning of the raw materials was poor, so that the product was badly off specifications (17-18-11) instead of (15-15-15). The Munson rotary, cylindrical rotary, and ribbon mixers gave good mixing. The concrete, cone and vertical tower mixers gave poor mixing, and sample analyses varied excessively from beginning to end of the discharge period.

Mr. Walter J. Sackett talked on New Sackett High Density Storage and Automated Bin Filling system. He explained how to get the most storage cubic ft. of space and loading and unloading bins with practically no segregation. He put across his message through slides and also told the gathering that his company has been issued patents on the subject. The next two papers dealt with technological improvements in bagging operation. With these improvements bags are now filled and handled at a rate of 1,200 per hour with an average of 1,000 bags per hour over a shift of 8 hours.

Elemental Phosphorus

Elemental phosphorus, it is believed in some quarters, will be a competitive source of P_2O_5 for fertilizers. Mr. Taylor Darden told the gathering regarding the production of phosphorus that it is still produced in conventional electric phosphorus furnace. The large size furnaces between 50,000 to 70,000 KW are being operated and produce 320 tons of P_2O_5 daily which is small compared to wet acid units at 1,300 tons P_2O_5 per day. But the electric furnace limit will be 150,000 KW or about 700 tons P_2O_5 per day per furnace. He informed that the T.V.A. and at least one commercial fertilizer company have been doing research on the reduction of phosphate rock in plasma furnaces. Also, there has been some work along this line by the use of hot gases in fluidized beds. Then he discussed the factors that may influence the selection of the elemental phosphorus route to phosphoric acid production for fertilizer use. Regarding transportation he said that it is when phosphorus instead of phosphate rock is exported, that presents the most interesting economic picture. The T.V.A. has prepared an analysis of the cost of importing phosphorus into India and then converting the phosphorus into diammonium phosphate vs. (1) wet process acid from imported rock and sulfur and then producing DAP and (2) importing DAP from the U.S.A. which shows that importing phosphorus is the cheapest.

Safety in the fertilizer plant, for that matter in any plant, pays well in insurance rates and indirect costs

from accident. Mr. John Mark educated the gathering on safety in the fertilizer plant. And with his talk session ended.

Micronutrients

The intensification of production practices has led in many farm areas to the rapid depletion of the native soil fertility elements and particularly of the trace elements. Interest in micronutrients is growing and the ways and means of replenishing them in deficient soils in a practical and efficient manner are under study. The third session devoted its first two talks to micronutrients. Mr. G. L. Bruton traced the history of development of fritted micronutrients at Ferro Corporation, Ohio and described the following process which is in operation.

From the batch mixer the material is dropped into a portable batch hopper which may either go to the compacting section or the smelting department. In smelting department raw batches containing all of the trace elements and other raw materials necessary to form the glass matrix are transported in the portable batch hopper to a 25 ton batch hopper feeding the smelter. This smelter is capable of melting special glasses at the rate of $2\frac{1}{2}$ tons per hour. The smelting takes place at approximately 2350-2500°F. The product, a homogeneous glass containing all the trace elements to be claimed, runs from the smelter into water. This quenching action shatters the glass into fine particles which drop to the bottom of the quench tank. A bucket elevator, perforated to release the water, elevates the wet frit to a fluid bed dryer. From the dryer again it goes into a portable batch hopper. The portable batch hopper is delivered from the smelter to an elevator which carries the dry frit to a surge hopper serving a cage mill pre-crusher. The pre-crushed material goes to a 20 ton milling storage hopper serving a vibrating steel ball mill. The fineness of the finished product is controlled by a Hardinge air swept fineness classifying system. Coarse materials are returned to the ball mill feeder and the end product goes to a Black Diamond bagger system or, if it is to be compacted, directly back to one of 1500 cubic foot storage bins serving the weighing and batching process. Then the material is granulated.

Mr. R. L. Gilbert, of American Cynamid Company explained the micronutrient coating process (trade name Microcharger) developed by his company. Micronutrients used in the tests were zinc, cuprous and manganese oxides, sodium borates and mixtures of these materials. Binders tested were fertilizer materials (such as ammonium nitrate, urea and non-pressure nitrogen solution),

sugars (dextrose and by-products of dextrose refining) and lignin sulphonate products. Fine micronutrient dust, preferably 90-95 per cent through a 200 mesh screen, was mixed with the blended fertilizer, and then binder solution was sprayed into the mixture. Samples for adhesion of micronutrient were tested by screening on 60 mesh vibrated by Ro-Tap for one minute. The —60 mesh material was considered to be all micronutrient. A period of 24 hours was allowed to elapse between preparation of the sample and testing for adhesion. Samples for caking were tested by sealing samples into small polyethylene bags and weighing them with 3.5-4 psi for 3 days. The degree of caking under this pressure was estimated qualitatively. Following are some of the results.

LABORATORY FORMULATION MICRO CHARGER
ON 6-24-24

Binder	Adhesion %	Caking in 24 hr.
Ammonium Nitrate	85	None
Ammonium Nitrate	87	None
NA Lignin Sulfonate	92	Slight
Dextrose	92	Slight

LABORATORY FORMULATIONS OF MICRO CHARGER

Binder Type	%	Micronutrient	
		Type	% by wt. Element
AN Soln, 64%	7.4	ZnSO ₄	20.4
		ZnO	1.2
AN Soln, 64%	10.4	ZnSO ₄	18.0
		ZnO	2.0
Enzose	2.1	ZnO	14.0
AN Soln, 64%	1.0	Na ₂ B ₄ O ₇	1.0

The 6-24-24 used as substrate in these tests was made from DAP, TSP, and Potash. The micronutrient dust was a mixture of zinc and manganese oxides and sodium borate, added to give 0.25 per cent each of Zn and Mn, and 0.06 per cent B. The amount of binder used was 1 per cent. All binder solutions contained 50 per cent solids. Three types of substrates were used in this work to make blends having nutrient ratio 5-4-0. The substrates were AN+ TSP, DAP+TSP, and Ammonium Sulfate+TSP. In all cases adhesion of micronutrient dust was over 97 per cent with little or no caking.

Cement and Sulphuric Acid from Calcium Sulphate

Dr. D. S. Ashburner discussed the production of cement and sulphuric acid from calcium sulphate by the Marchon process. The reactions in the process consist first of a reduction step where carbon in the coke reacts with one quarter of the calcium sulphate to form calcium sulphide. The second is a decomposition step where the calcium sulphide previously formed now reacts with the rest of the calcium sulphate at a somewhat higher temperature to form sulphur dioxide and calcium oxide. Then follows the Clinker reaction where the calcium oxide combines with silica, alumina and iron oxide present in the other raw materials to form the compounds which make up ordinary Portland cement (e.g. tricalcium silicate, dicalcium silicate, tricalcium aluminate and ferrite compounds etc). The main difference between this Marchon process and conventional cement technology lies in the closer control that is needed at each stage of the process. The raw material mixture has to be accurately proportioned and the temperature and firing conditions in the kiln have to be closely controlled. For instance if the temperature in the firing zone becomes just that bit too high the material will melt causing "flushes" and consequent damage to the kiln lining. Excess CaS can also result which produces a poor cement clinker. If the atmosphere in the kiln becomes reducing, quantities of sulphur can be deposited in the gas cleaning equipment causing serious operating and maintenance problems in those areas.

For the production of one short ton of 100% sulphuric acid the following utilities (approximate) are required.

Anhydrite	1.6 to 1.7 tons
(or Gypsum	2.0 to 2.2 tons)
Shale	0.29 tons
Sand	0.06 tons
Coke	0.10 tons
Fuel	6 million Btu's Anhydrite (10 million Btu's Gypsum)
Cooling water	14,000 gals. (Circulating)
Electricity	190 kWh up to clinker production, 38 kWh for cement grinding

Nitrophosphate

Mr. Raymond Ewell gave the opening talk on "Economics of Nitrophosphate Fertilizers" in the first session. In his opinion nitrophosphate is a very complex subject, one surrounded by much mystery, many prejudices and mental fixations. Nitrophosphates contain a lot of nitrate nitrogen—usually 40 per cent to 45 per cent

of the nitrogen is in the nitrate form and 55 per cent to 60 per cent in the ammonium form. When nitric acid is the sole or principal acidulant a lot of nitrate is inevitable. This in the opinion of the author is no handicap in most countries since nitrates are widely used fertilizers: but there is some evidence—not fully convincing—that nitrate nitrogen has a significantly lower fertilizer efficiency on paddy rice than ammonium forms of nitrogen, such as urea, ammonium sulfate, ammonium chloride or ammonium phosphate. This loss of efficiency is believed to be due to loss of nitrogen resulting from bacterial decomposition of nitrate ions in the anaerobic conditions existing in underwater culture as in paddy rice. This would tend to indicate against the use of nitrophosphate fertilizers in areas where rice is a major crop. However, it may be pointed out that two of the largest fertilizer plants in India—Nangal and Rourkela—produce only ammonium nitrate and that in the United Arab Republic calcium nitrate and ammonium nitrate are the only nitrogen fertilizers produced. It should also be remembered that paddy rice is only one of many crops even in Southeast Asia. Nitrate fertilizers are quite suitable for wheat, corn, cotton, sugarcane, peanuts, beans, jute, tea, coffee, cocoa, rubber, tobacco, coconuts, potatoes, bannas and many other crops of the tropical zone. Even the usefulness of a nitrate fertilizer in a rice-growing area is purely a matter of economics, maintained the speaker. His argument is, if a nitrate fertilizer is enough cheaper than a non-nitrate fertilizer, then it is economical to use it. For example, if a nitrophosphate

fertilizer should have 90 per cent of the fertilizer efficiency of an equivalent non-nitrate fertilizer, such as urea-DAP, and the nitrophosphate was priced at 90 per cent of the price of the non-nitrate fertilizer, they would be then economically equivalent.

He described two processes: Calcium Nitrate Crystallisation Process (CNXlzn) and Ammonium Sulphate Recycle Process (AS Recycle) both are capable of producing N-P fertilizers with WSP greater than 75 per cent and using nitric acid as the only acidulant. Two plants are now operating and one is under construction using the CNXlzn process. The AS Recycle process, in several variants, is being offered by several engineering contractors, but so far no plant has been built. Then he gave an outline of the process and said that the choice of the process will depend upon existing or potential market, competitive processes, relative capital costs and price of sulphur at particular location (if a sulphur using process is being considered). Then he made the following economic comparison among the three processes, as shown in the Table below.

In his call "Save Sulphur—Use Nitrophosphate" Mr. B. A. Dumain of Power-Gas Corporation of America described in detail the Dutch State Mines/Power Gas process capable of producing water soluble P_2O_5 content up to 95 per cent and drew the conclusion that excluding the common ammonia and nitric acid facilities NP/ASU plant cost 15-20 per cent less on turn-key, battery limit basis than sulphur based conventional plant. He conclu-

PRODUCTION COSTS PER METRIC TON OF 28-14-0

	CNXlzn Process	AS Recycle Process	S/AA/PA Process	Prices of Input
Capital investment*	\$8,000,000	\$8,000,000	\$7,500,000	
Inputs:				
Phosphate rock	\$4.27	\$4.27	\$4.27	\$10/MT
Nitric acid	8.12	8.12	8.33	\$14/MT
Ammonia	6.00	6.00	5.85	\$30/MT
Sulfur	—	—	4.05	\$30/MT
Gypsum	—	.60	—	\$ 5/MT
Steam	.40	.60	—	50cent/MT
Electric power	.80	.70	.60	1cent/kWh,
Fresh water	.20	.20	.20	20cent/Mgal
Cooling water	.40	.40	.40	5cent/Mgal
Costs based on investment 30% of investment per year	5.10	5.10	4.80	
	\$25.29	\$25.99	\$28.50	

*Plant size is 1430 MT/D or 472,000 MT/Y of 28-14-0.

Capital investment for turnkey battery limits plant, not including land, raw material storage, product storage, bagging, shipping, off-sites, or working capital.

Each \$1 million in capital investment changes production costs per ton of 28-14-0 by \$ 0.635 on basis of 30% of investment per year.

ded his paper by saying that NP/ASU plant will operate continuously for over 335 days per year. This allows close integration with the ammonia and nitric acid facilities while at the same time minimising intermediate storage requirements. It will also utilize a substantial amount of already installed equipment in a conventional sulfuric acid based factory complex, i.e. plant conversion to NP/ASU may be possible depending on individual circumstances. Where wet phosphoric acid plant is installed the ASU plant will provide a disposal unit for noxious by-product gypsum effluent. If the ammonium sulfate section is enlarged it will provide a relatively cheap gypsum to ammonium sulfate facility to make straight N-fertilizers such as 21:0:0 or 26:0:0. A small increase in the capacity of the ammonium sulfate section can enable up to 15 per cent of the sulfuric acid requirement of an adjacent wet phosphoric acid plant to be saved, the saving being effected by substitution of ammonium sulfate. The criticisms of the NP/ASU process having high capital cost showed the author in the table of capital costs included in his paper negates this.

Then Mr. S. Strelzoff described the Chemico Nitrophosphate process. The Chemico process starts with the digestion of phosphate rock with sufficient nitric acid to convert all the rock phosphate into phosphoric acid. Fifty to sixty per cent nitric acid is used to control the water content of the slurry, which is then mixed with a (38-40%) ammonium sulfate solution. The latter reacts with the calcium nitrate to produce calcium sulfate dihydrate (gypsum). The gypsum is separated from the mother liquor, which is principally phosphoric acid and ammonium nitrate with small amounts of iron, aluminium, magnesium, calcium, fluorine as well as vanadium and rare-earth metals present in the phosphate ore. The gypsum is washed free of phosphate and is sent to the ammonium sulfate plant where it is treated with ammonium and carbon dioxide; the gypsum is converted to ammonium sulfate and a calcium carbonate precipitate. When filtered from the liquor, the calcium carbonate can be dried and used as agricultural lime or mixed with ammonium nitrate to make nitro-chalk (ammonium nitrate-lime stone fertilizer having a 20 to 26-0-0 grade, which is extensively used in the European countries to increase the yield of forage crops on grazing land). The purpose of limiting the nitrogen content to 20 to 26 per cent as compared to pure ammonium nitrate with 34.5 per cent nitrogen is to reduce the hygroscopic capacity and minimize the fire hazard of the product.

The ammonium sulfate liquor, having 38 to 40 per cent concentration, is recycled to the precipitator where calci-

um, solubilized by the reaction of nitric acid with the phosphate rock, is removed. Since 95 to 98 per cent of the gypsum is converted to ammonium sulfate and a small excess of ammonium sulfate is required for complete precipitation of the calcium, a cheap source of make up gypsum or ammonium sulfate is required. In concentration crystallization step the mother liquor product of the gypsum separation is ammoniated to a pH of about 3.5 for the conversion of the phosphoric acid to monoammonium phosphate. The solution which now contains about 58 per cent water must first be concentrated to 20 per cent water and fed to a vacuum crystallizer. With proper design, the monoammonium phosphate is produced as crystals that are easily separated from the ammonium nitrate.

Regarding the economics he said that the cost of producing equal amounts of plant nutrient by the Chemico process and the DAP plus ammonium nitrate routes are the same when sulfur price is \$ 32 per long ton or more. For the mixed acid phospho-nitric route, the break even point is considerably high. Variations in ammonia cost only reflect changes in total product cost, while variations of sulfur cost reflect increased advantage for the Chemico process. Then he told that Chemico has developed and laboratory tested number of processes based on partial neutralization of the liquor produced by reacting phosphate rock with nitric acid and ammonia to precipitate calcium phosphate. Then he narrated some modifications on this basic process which removed the basic deficiencies in the process.

Mr. W. A. Lutz of Weston Process Design in his talk "Nitrophosphates, Fact, Fiction and Philosophy" surveyed the various characteristics of nitrophosphate like water solubility, product grade, nitrogen to potash ratio, calcium nitrate utilization, prilling or granulation, storage, handling, quality, ratio of ammonia and nitrate nitrogen, product cost etc. His observation is that the historic objections to nitric phosphate fertilizers would be difficult to defend in the light of recent practice and experience. Complex fertilizers being produced by this route in Europe are superior to the majority of equivalent compounds made in the United States with respect to total grade and water solubility. It is also highly probable that they are superior in some of the less tangible areas such as product quality, storage and handling characteristics. The opportunities for cost reduction appear to be excellent but detailed cost comparisons are necessary to firmly establish overall differences. A large potential market does exist for fertilizers which can be made using this type of process. The selection of processes to be used in a new or moder-

nized installation is a difficult and complex problem. Nitric phosphate processes do merit full consideration, along with other technical developments, in this progressive and expanding industry. As with most other developments, they do not represent a universal solution to all the problems in the industry. There does appear to be a place for them and with this hope the third session ended.

Mr. W. E. Brown presented the paper Nitric Acid Digestion "Nitrophosphate" Process co-authored by R. F. McFarlin. He pointed out that a question whether the nitrophosphate process is competitive with DAP is meaningless because the DAP plant is a P_2O_5 process which necessarily produces nitrogen while nitrophosphate process is primarily a nitrogen process which produces some P_2O_5 . The choice of the nitrophosphate plant is favoured by the two factors viz. whether the producer has an ammonia plant and consequently a source of free carbon dioxide and whether he has a market for products such as 28-14-0, 23-23-0, 20-30-0 and ammonium nitrate.

In the basic process, narrated the author, phosphate rock is digested with a mixture of nitric acid and ammonium sulfate. The resulting slurry contains gypsum and a solution of ammonium nitrate and phosphoric acid. The gypsum is filtered and the solution is further treated accordingly to the desired final product. A product having an N/P_2O_5 ratio of about 2 is made by simultaneously ammoniating and concentrating the filtrate and granulating the resultant slurry. Low N/P_2O_5 ratios are manufactured by separating part of the ammonium nitrate before neutralization. These low N/P_2O_5 ratio products yield ammonium nitrate as a co-product. The gypsum is reacted with ammonia and CO_2 to form calcium carbonate and ammonium sulfate solution. The solution is filtered from the chalk solids and recycled to the rock digestion system. The various steps like rock digestion, gypsum filtration, filtrate evaporation, ammonium nitrate crystallization, ammonium nitrate centrifugation, neutralization, concentration, gypsum ammonium-carbonation, chalk filtration etc. were described in detail by the speaker. One modification of the NAD process involves substitution of potassium sulfate for all or part of the ammonium sulfate in the attack solution. This replaces ammonium ion in the final product with potassium and results in lower N/P_2O_5 ratios without separation of ammonium nitrate from the digestion liquor. These N-P-K grades contain potassium nitrate rather than the conventional potassium chloride. The lowest N/P_2O_5 ratio product which can be obtained by crystallizing potassium nitrate at ambient temperatures analyzes about 17-34-17. In this

modification the total amount of nitrogen in the combined products is about equal to the total P_2O_5 . The principal advantage of this process is that by extracting the ammonium nitrate from the basic nitrophosphate mix, practical ratios can be made and the economics, therefore, have real significance. It still has, pointed the speaker, some of the nitrophosphate limitations, but he felt that many possibilities have been opened up by this improvement and that the fertilizer industry should evaluate this opportunity to modernize its nitrogen and P_2O_5 manufacture.

Mr. Sheldrick while commenting on nitrophosphate discussion complained that these nitrophosphate papers are usually presented by engineering companies or academics, who don't have to operate fertilizer plants, and they usually finish up by saying there is some lack of flexibility. What they don't tell is what this is worth in economic terms. He further pointed out that in Europe, which is traditionally the home of nitrophosphate processes, there are more people who are changing from nitrophosphate process to the phosphoric acid route than there are people who are building new nitrophosphate plants.

Monoammonium Phosphate

Mr. Hemsley of Fisons Limited, discussed the new Fisons process known as MINIFOS for powder monoammonium phosphate, a high analysis material containing sixty units or more of plant food nutrient. The process has two basic steps. The first involves the pressure ammoniation of wet process phosphoric acid and solution. The second step is the flash drying of the solution to a powder material suitable for use as phosphate donor in conventional granulation plants. The manufacturing process is simple, cheap and efficient, whilst the product is compatible with all other fertilizer raw materials, including urea. As it can easily be transported in bulk the phosphate rock producer may find it as a cheaper and simpler way of transporting P_2O_5 than either phosphate rock or concentrated phosphoric acid.

Ammonium Polyphosphate

Some years back, it was discovered that high-temperature concentration of phosphoric acid solutions would not only remove free water, but a good deal of the molecular water as well to result in condensed or polymerised phosphates of considerably higher phosphate contents than the customary ortho form. TVA and others developed special evaporators to produce these superphosphoric acids, which could be ammoniated to form solid

or liquid ammonium polyphosphates. In the last session three papers dealt with ammonium polyphosphate. Dr. Ronald D. Young of TVA described and compared the several alternative schemes for the production of ammonium polyphosphate material. By one scheme the granular ammonium polyphosphate (15-61-0 or 15-62-0), introduced by TVA, is produced by ammoniating electric-furnace superphosphoric acid in a pressure reactor. In another scheme envisaged the usual merchant-grade wet-process acid (containing about 54 per cent P_2O_5) is ammoniated in two-stage reaction system. The heat of reaction of anhydrous ammonia and the acid is utilized effectively to evaporate water. Mr. Frank P. Achorn of TVA discussed the uses of solid ammonium polyphosphate in bulk blending, granulation and fluid fertilizers. He described the product in detail, pointed out its production in clean liquid, suspension and bulk blending fertilizers and briefly discussed its use as a

granulation aid. Regarding the agronomic characteristics of the product he said that the material is suitable for either broadcast application or band placement to the side and below the seed. Ammonium polyphosphate can serve as an effective carrier of some micronutrients e.g. granular ammonium polyphosphate is a more effective carrier of zinc (as zinc oxide) than granular monoammonium phosphate.

The paper "fluid fertilizer containing polyphosphate" presented by R. E. Formaini of Applied Chemical Corporation gave micronutrient solubility data for boron, copper, iron, molybdenum, manganese and zinc in fluids containing wet-process 10-34-0, urea-ammonium nitrate solution and muriate of potash. And with this paper the 18th Annual Meeting of Fertilizer Industry Round Table ended.

[S. A. Kulkarni]

Notes & News

World's Largest Ammonium Nitrate Plant

The largest ammonium nitrate production capacity (1.2 million tpa) has been brought fully on stream as part of an expansion to the existing chemical complex at Pilaury (Poland). For this venture Polimex (the Polish foreign trade corporation) had signed contract with Haldor Topsoe (Denmark), Simon Carves (UK), Voest (Austria) and Kolteubach (France) for construction of facilities to produce ammonium nitrate and urea.

The project was to produce a guaranteed 3,345 tpd of prilled ammonium nitrate (rated capacity 3600 t) from liquid ammonia and 55 per cent nitric acid and also to provide storage, bagging and dispatch facilities in three 1200 tpd production streams. In each of the streams, which together occupy an area of 5290 m², the nitric acid is neutralized with gaseous ammonia in two 600 tpd operating at 3.5 kg/cm² and the resulting solution is preliminarily evaporated to 95 per cent in two 600 tpd cascade type evaporators operating under a vacuum of 0.2 kg/cm². After evaporation the 95 per cent solution is passed to a single mixing vessel which serves both to homogenize the solution and also to dissolve recycled fines. Before prilling, the solution in each production stream is finally evaporated in four prilling film evaporators, operating at atmospheric pressure and employing countercurrent hot air as the drying agent. Prilling takes place in a square tower measuring 12m × 12m × 30m. in height, incorporating at the top a static nozzle-type prilling device. The prills are then cooled from the prilling temperature of 110-115°C down to at least 30°C in a fluidized bed cooler. Cooling and fluidizing air for this is initially dried and cooled in a heat exchange system using liquid ammonia. The operation provides all the gaseous ammonia required by the process together with, under certain atmospheric conditions, excess gaseous ammonia at low pressure which is recovered by reliquefaction in the adjacent ammonia synthesis installation. After cooling the product ammonium nitrate is screened and fed by a belt conveyor to a coating drum before storage.

Each of the three product handling systems consists of eight 200 te automatically-filled, intermediate storage hoppers, which constitute a maximum storage capacity of 1600 te, discharging into an equal number of bagging units, equipped with sewing and fusing devices to deal with both paper and plastic sacks. These bagging units can each accommodate upto 40 tph from the storage hoppers.

[*Nitrogen*. No. 58, (1969), 371]

Acetic Acid Via Methanol and Synthesis Gas

Reaction of methanol and carbon monoxide to produce acetic acid was thought uneconomic. But Badische Anilin & Soda-Fabrik AG (Ludwigshafen, W. Germany) has turned this reaction into commercial operation. BASF reports that of every 100 lb. of 99.8 acetic acid, about 50 per cent is propionic acid. The rest is a mixture of ethyl and butyl acetate and 2-ethylbutanol, which serves as an entrainer in the dewatering of crude acetic acid. The process is as follows.

At Ludwigshafen, liquid methanol feed first passes through a wash column and a mixing tank before entering the reactor. In the mixing tank, the methanol picks up the required amounts of water and recycling catalyst. Thus, feed to the reactor—a shaft furnace lined with Hastelloy C—is a compressed CO stream entering at the bottom plus the recycle mixture supplied to the top of the unit.

The reactor has a high thermal capacity, and since no strongly exothermic reactions take place, it is possible to keep temperatures (and therefore, conversion levels) constant for long periods. A preheater in the recycle line makes up the small thermal difference between the 1.9 million Btu/ton of acid product released in the reactor, and the heat required to bring reactants up to the desired temperature (482°F.). Mixing inside the reactor is promoted by an internal recycle loop that is powered by incoming gas.

Crude product and unreacted gas emerge from the top of the reactor and pass through a cooler, on their way to a low-pressure separator. Here, the stream is

flashed to 75-150 psi. Flashed vapor contains methyl iodide from the catalyst; in order to recover the iodide, the gaseous stream emerging from the top of the low-pressure unit is washed with incoming fresh methanol in the wash column. Residual gases (CO, CO₂ and CH₄) leaving the wash column can be recovered for their heating value, which is one-third that of natural gas.

Methanol, reactant gas and part of the catalyst pass from the bottom of the wash column to a mixing tank. Here, they are joined by water, more catalyst and recovered by-products. The mixture is recycled to the reactor.

It takes five columns to convert the crude acid leaving the low-pressure separator into high-purity product. First, a degasser distills off volatile components such as acetaldehyde, methyl formate, methyl iodide and part of the methyl acetate. These are sent back to the mixing tank.

Acetic acid, catalyst and some by-products go from the degasser to a small catalyst-separator that removes cobalt iodide as a concentrated acetic acid solution. After iodide removal acetic acid and heavier by-products pass to the dewatering column.

According to BASF, catalyst recovery—an important factor in overall economics—is excellent. Since the Ludwigshafen plant has been on stream, catalyst has been cycled about 10,000 times through the purification section; recovery has been practically 100%. Iodine losses in the wash column are negligible.

Due to the high water-content of the acetic acid stream leaving the catalyst separator, azeotropic distillation is used for final acid purification. Acid enters the dewatering column in vapor form, and a mixture of water, formic acid and various by-products rises to the top of the column. This mixture condenses in two phases, and the upper phase, which consists of alkyl acetates and some 2-ethylbutanol, is recycled as an entrainer (its entraining power is roughly equal to that of n-propyl acetate).

Free of water and formic acid, the acetic

acid stream passes from the dewatering column to a final purification column that removes the usual 4% of high-boiling byproducts and yields better than 99.8% acetic acid. Large plants would benefit from the further recovery of propionic acid, which accounts for about half of the residue leaving the bottom of the acetic acid column; this is done in the residual column.

Acetic acid yields are 90% based on methanol feed and 70% based on CO feed. About 3.5% of incoming methanol leaves the system as methane, 4.5% as liquid by-product and 2% is lost in waste gases. As for the CO feed, some 10% of it is converted to CO₂.

BASF says that similar results can be obtained using crude rather than pure methanol as starting material. At Ludwigshafen, up to 70% of the methanol feed has been replaced at times by dimethyl ether produced during methanol synthesis.

[*Chem. Engng.* 76 (11) (1969), 148]

Oil and Chemical Situation in India

In a recent statement, the Union Ministry of Petroleum and Chemicals has shown that the crude production by Oil and Natural Gas Commission and Oil India Ltd has risen from 2 million m. tonnes (1964-65) to 5.94 millions in 1968-69, while the demand of petroleum products (1968-69), was of the order of 15m. tonnes. This demand will progressively increase to about 26.68 and 31.75 million metric tonnes in 1973 and 1975 respectively. To be self-reliant the country will have to produce about 35 million tonnes of crude in 1975, against this the production is estimated to rise to about 12 million tonnes according to the present projections. The widening gap between the indigenous production and consumption of oil will mean a serious drain on foreign exchange resources. Strenuous efforts should therefore be made for production of more crudes indigenously.

It is estimated that there are one million sq. km. of sedimentary areas in the country and so far an area approximately 42 per cent thereof has been covered by the various geological and geophysical surveys and drilling operations have been undertaken over only a part thereof.

However, there is reason to believe that there are voluminous oil resources in off-shore areas, so a sound order of priority will have to be followed and most promising area where oil finds are likely to be large

and readily available should receive priority. The surveys and exploration drilling will have to be stepped up with a view to increase production. With this end in view ONGC has drawn up a 10-year tentative plan comprising geological, geophysical and drilling activities to achieve the following objectives to find 85 m. tonnes of additional initial recoverable reserves on-shore and additional 115 m. tonnes of initial recoverable reserves of oil; to establish oil production of 14.5 m. tonnes/yr. by 1978-79. and gas production rate of about 900 m. cu. metres/yr.

The financial outlay for carrying out the above programme is as follows: Rs. 403.27 crores during 1969-74 and Rs. 805.50 crores during 1974-79.

Oil India Ltd., has a programme at a continuous rate of m. tonnes till 1978. It has also embarked on further exploration in other areas within its leased areas. The recent oil show in Kusijan area shows a possibility of further increase in OIL's output within the next few years. The Assam Oil Co. has also embarked within its Digboi lease area on additional production.

ONGC has located certain promising structures on the West Coast and Russian experts will be making a project report on off-shore drilling on Aliabet structures. Regarding deep water drilling on Bombay High structures, the Commission has to take expert advice.

Refinery Capacity: For the first time in 1967, India has reached self-sufficiency in all the major petroleum products except kerosene, and with commissioning of Madras refinery, the country's refining capacity will rise to 20 m. tonnes. With the 10th refinery at Haldia and expansion of Koyali and Nunmati refineries the refining capacity will rise to 235 m. tonnes. According to a report by Indian Institute of Petroleum the country's demand of all petroleum products by 1975 will be around 32 m. tonnes. A Study Group is examining the question of future additional refining capacity that will have to be created in the foreseeable future in terms of IIP's report.

Government has approved of 3 projects at Bombay, Madras and Calcutta for producing 7-8 m. tonnes of base raw materials for lubricants. It is anticipated that by 1972 bulk of the requirement of the lubricant base stocks would be produced indigenously.

The Marketing Division of IOC handled in 1968 about 43% of the total consump-

tion (about 15 m. tonnes) of petroleum products and is gearing itself to increase the sales in the coming years. With the addition of Madras and Haldia refineries, the public sector's participation in refinery processing will increase to about 70 per cent by 1975.

The country is self-sufficient—rather surplus—in motor gasoline, naphtha diesel, furnace oil, petroleum coke and wax but is still deficient in kerosene, aviation gasolines and base stocks of lubricants; the foreign earning on the above surpluses were Rs. 14 crores including the fuels sold at international air ports. However naphtha may become a deficit product if all the naphtha based projects reached the stipulated production.

An informal price control scheme of petroleum products based on import-parity basis came into existence since 1961 after the recommendations made by Damle Oil Prices Enquiry Committee. After 3 years another committee named Working Group on Oil Prices made certain discounts on crude and product prices in February 1966. However a re-examination of the marketing and distribution cost of the oil industry is early warranted, and therefore a new committee headed by Sri Shantilal Shah M.P. has been working since June 1968 on the products pricing. Among other things Shah committee will recommend a suitable pricing basis, the quantum of marketing and distribution charges and projects of the marketing operations.

Petrochemicals: With the completion of the first phase of implementation of petrochemical projects, the implementation of the second phase has been taken in hand. The Rs. 20-crores public sector petrochemical project in Gujarat has been approved and approval has been granted to further private sector plants with a total investment of Rs. 32 crores. Scrutiny of further proposals with an investment of Rs. 50 crores is in an advanced stage. A detailed study has been commissioned for the erection of a synthetic rubber plant in public sector.

Fertilizers: 1968-69 began with an installed capacity of 849,000 and 410,000 tonnes of nitrogen and P₂O₅ which by the end of the year stood at 1,024,000 and 410,000 and the actual production for the same year was 545,000 and 210,000 tonnes respectively. The production in 1969-70 is expected to rise to 850,000 and 310,000 tonnes of N and P₂O₅ respectively; this year is a crucial one for the success of the IV plan, since fertilizer plants take 4-5

years to materialize. In an attempt to maximize the utilization of indigenous raw materials, the Ministry decided to go ahead with 3 coal-based plants, of which field work will begin on two of them before the end of this year. Attempts to tie up the the needed foreign exchange are in progress, and in this regard a well-known-colliery owner and a foreign consortium of engineering firms have shown interest for establishing a coal-based fertilizer plant in Maharashtra.

The Government have decided to put up a fertilizer factory in the public sector based on imported ammonia as part of a broad programme of economic and industrial cooperation between Iran and India. The World Bank has agreed to consider favourably India's request to assist selected public sector projects and the Bank's team is expected to make an appraisal of the Nangal expansion and Cochin phase II. The Ministry has appointed a working group to study the development of the deposits of pyrites and rock phosphate recently discovered in Rajasthan.

Pesticides: Adequate capacities have been created in respect of most of the pesticides, viz. parathion, malathion, fungicides, rodenticides and fumigants, so the main emphasis in the coming years will be on the stabilization of production in consonance with demand. Steps have been taken to create additional capacities of DDT (present capacity 4200 te/yr at HIL Delhi) and BHC. HIL has been asked to set up additional capacity of 7000 te/yr near Panvel, close to the facilities of HOC. Regarding BHC the Government have decided to consider the establishment of 3 more units each of 3000 te capacity in addition to the 4 plants adopting chemi-anlagen technology of E. Germany with a total capacity of 12,000 te for which letters of intent had been issued; the total capacities under production and implementation at present are 26,650 tonnes while the target for IV plan is 50,000.

[*Oil Commentary*, 6 (21-22) (1969), 9]

Patents*

Ammonium Nitrate Stabilization: R. F McFarlin and D. E. Brown (to USS Agri-Chemicals, Inc.).

*These patents have been reproduced from *Fertilizer Abstracts* published by the National Fertilizer Development Centre, TVA Muscle Shoals, Alabama (U.S.A.) with kind permission of the Editor of FA.

—Editor

U.S. 3,428, 418, Feb. 18, 1969, Appl. June 27, 1967; 5 pp.

Prilled NH_4NO_3 is stabilized against phase transition by incorporating $\text{Mg}(\text{NO}_3)_2$ or $\text{Ca}(\text{NO}_3)_2$ in the melt before prilling. It has been known that $\text{Mg}(\text{NO}_3)_2$ and $\text{Ca}(\text{NO}_3)_2$ modify the crystal habit of NH_4NO_3 so that the phase transition that normally occurs at 32° is shifted to about 55° . It is difficult however to prepare a mixture containing the dehydrated additives by usual methods. In the present method, chemical grade MgO (or CaO) is added to molten NH_4NO_3 in proportions to give a mixture containing 15-45% $\text{Mg}(\text{NO}_3)_2$. The mixture is held at $170-200^\circ$ to complete the reaction while collecting evolved NH_3 . The resulting melt is then metered into molten NH_4NO_3 to give a mixture containing at least 0.2% MgO and preferably 0.2-0.4% MgO . Prills produced from the mixture are stabilized against the 32° phase transition.

[*Fertilizer Abstracts*, 2(4) (1969), 69]

Ammonium Nitrate-Calcium Carbonate Fertilizer: Leonard W. Zahnstecher (to Foster Wheeler Corp.).

U.S. 3,421, 878, Jan. 14, 1969, Appl. Apr. 6, 1966; 3 pp.

Prilling of $\text{NH}_4\text{NO}_3\text{-CaCO}_3$ mixtures is difficult because minor decomposition and resulting evolution of NH_3 causes foaming that interferes with flow of the molten mixture through the holes in the prilling basket or spray head. In the process described, a small amount of $(\text{NH}_4)_2\text{SO}_4$ or K_2SO_4 (0.2-3.0%) added to the melt before prilling effectively suppresses foaming. In an example, a mixture of 60% NH_4NO_3 (containing 4% H_2O) and 40% CaCO_3 at 281°F . developed a surface foam layer over 12 in. deep. Under the same conditions but with 1% $(\text{NH}_4)_2\text{SO}_4$ added, the foam layer was only 4.5 in. deep.

[*ibid*, 69]

Ammonia Synthesis: W. A. Bulen (to Kettering Scientific Research, Inc.).

U.S. 3,423,289, Jan. 21, 1969, Appl. Oct. 11, 1965; 7 pp.

An organo-metallic catalyst for the reduction of N gas to recoverable NH_3 is derived from N-reducing micro-organisms (for example, various species of *Azotobacter*) by rupturing the cells, removing the solid components and separating the nucleic acids from the active soluble fraction. The active catalyst material is removed from a mixture of solubilized proteins of net

negative and net positive charges by precipitation with protamine sulfate followed by liberating the active material by treatment with cellulose phosphate without destroying the activity of the catalyst. Thus, in the absence of cell components required for carbohydrate metabolism the catalyst is operative at atmospheric temperatures and pressures in the presence of a phosphorylating agent and a synthetic electron donor to continuously reduce gaseous N to recoverable NH_3 . The catalyst includes metallic functional groups such as Fe and Mo. The method is not dependent upon a living system and substantially all the NH_4 ions produced as a result of the chemical reduction of N gas are recoverable as NH_3 rather than being consumed biologically in the synthesis of amino acids.

[*ibid*]

Slow-Release Nitrogen Fertilizer: Charles Kapar (to W. R. Grace & Co.).

U.S. 3,427,144, Feb. 11, 1969, Appl. Oct. 7, 1965; 2 pp.

A mixture of 70-98% urea and 2-30% nitrilotriacetonitrile is prepared by melt blending of the ingredients at 133° . The minimum time necessary to obtain a uniform blend is used. The melt is then cooled, solidified, and comminuted to an appropriate size for use as a slow-release fertilizer. The retardation of the rate of dissolution ranges from 4% for a mixture containing 2.2% nitrilotriacetonitrile to 17% for a mixture containing 29.8%

[*ibid*, 70]

Production of Phosphates from Phosphatic Slimes: Wayne C. Hazen, Angus V. Henrickson, and Pablo Hadzeriga (to Hazen Research, Inc.).

U.S. 3,425,799, Feb. 4, 1969, Appl. Aug. 14, 1964; 9 pp.

Waste slimes from the beneficiation of Florida or western phosphate rock are slurried in H_2O to give a solid concentration of about 10% by wt. The suspension is heated to $60-70^\circ$ and H_2SO_4 is added slowly (≥ 2 hours) at a steady rate in an $\text{H}_2\text{SO}_4\text{:P}_2\text{O}_5$ wt ratio of 2-2.8:1. The reaction mixture is filtered, the presence of large crystals of gypsum from the reaction serving as a filter aid. Filtration rates are 300-400 lb wet filter cake/sq ft/24 hours using polypropylene multifilament will cloth and 15-18 in. Hg vacuum. The filtrate containing about 16g P_2O_5 /l. is passed over a cation exchange resin in the H form such as "Dowex 50W-X8" to

remove Fe and Al impurities that would interfere with the next step. The solution is then extracted with an amine solvent such as "Alamine 336" which dissolves the P_2O_5 . The P_2O_5 is recovered from the solvent by treatment with NH_3 to prepare crystalline ammonium phosphate as product.

[*ibid*, 71]

Superphosphoric Acid: B. J. Young (to Union Oil Co.).

U.S. 3,420,627, Jan. 7, 1969, Appl. Jan. 21, 1964; 5 pp.

Vacuum evaporation is followed by submerged combustion evaporation in the manufacture of anhydrous phosphoric acid containing condensed polyphosphoric acids. Dilute wet-process H_3PO_4 containing 27-63% P_2O_5 (impurity-free basis) is fed to a film-type vacuum evaporator where the concentration is increased to 69-73% P_2O_5 . The product of the vacuum evaporator is fed to a submerged combustion evaporator where it is contacted with hot gases at 1000-2000°F., increasing the concentration to 73-82% P_2O_5 (impurity-free basis). The equipment is smaller than required for either evaporation method when used alone, and there is little interference from scaling in the vacuum unit.

[*ibid*, 72]

Superphosphoric Acid: R. F. McFarlin and W. A. Satterwhite (to Armour Agricultural Chemical Co.).

U.S. 3,423,173, Jan. 21, 1969, Appl. Dec. 8, 1965; 4 pp.

Polyphosphoric acid is produced by spray concentration of wet-process H_3PO_4 . In an example, impure H_3PO_4 containing 54.26% P_2O_5 was fed through a Bowen SW-type atomizing nozzle into the upper part of a spray chamber. Hot combustion gases from a propane burner, tempered with air to 940°F., were fed tangentially into the upper part of the spray chamber. The acid feed rate was 300 ml/minute; the inlet gases leaving the spray chamber were passed through a cyclone collector which separated acid droplets, and then through a feed acid preheater and a wet scrubber. The product acid contained 68% P_2O_5 and so solids. Higher concentrations of product acid can be obtained by increasing the gas outlet temperature (to 475°F) and by recycling the acid.

[*ibid*, 72]

Superphosphoric Acid: Clyde Reeder.

U.S. 3,425,478, Feb. 4, 1969, Appl. Dec. 11, 1967; 6 pp.

Hot combustion gases and H_3PO_4 are passed concurrently through a tube cooled at the inlet end. The residence time is less than one second and the liquid is discharged from the tube at substantially the same temperature at the gases. The tube is discharged to an open vessel where the product acid separates from the gases and vapors. In an example, the apparatus was comprised of a Type 316 stainless steel tube 0.5 in. in diameter and 42 in. long. The first 12-in. portion of the tube was cooled by a water-jacket; the remainder was thermally insulated. Hot gases from the combustion of 36 standard cu ft/hour of CH_4 were fed into the inlet end of the tube. Acid containing 54% P_2O_5 was introduced into the tube at a point 10 in. from the inlet end at 9.7 lb/hour. The mixture was discharged from the tube at 580°F. and the product acid, containing 76.2% P_2O_5 and 0.4% insolubles, was separated from the gases and vapors. There were no deposits in the tube after 8 hours of operation. Similar tests made without cooling of the tube gave product of lower purity. In comparison with the usual submerged combustion method for producing superphosphoric acid, the present method requires less expensive equipment, operation is simpler, the heat economy is better, and the product acid is purer.

[*ibid*, 72]

Wet-Process Phosphoric Acid: Norman Robinson (to Fissons Fertilizers Ltd.).

U.S. 3,418,077, Dec. 24, 1968, Brit. Appl. Feb. 12, 1965; 3 pp.

Phosphate rock is acidulated in two stages. In the first stage an excess of Ca ions is present, providing a greater number of dissolved Ca ions than dissolved SO_4 ions at all times in the first stage. In the second stage an excess of SO_4 ions over Ca ions is provided, resulting in a slurry of calcium sulfate hemihydrate in concentrated H_3PO_4 which is readily filterable to yield 45-55% P_2O_5 acid. For example, Morocco phosphate rock (P_2O_5 33.4%, CaO 51.2%) was fed at 17 parts/hour to a first-stage acidulation vessel supplied with recycled slurry containing 2% dissolved SO_4 at 274 parts/hour. The recycled slurry was a mixture of slurry from the second acidulation, "strong acid", and "wash acid" from the gypsum filter. The temperature in the first acidulation vessel was 100°, and the amount of SO_4 was such that 30% of the Ca in the rock was precipitated as $CaSO_4$. The slurry was fed to a second vessel with 16 parts/hour of 96% H_2SO_4 ,

providing a 1% excess of H_2SO_4 over that required to convert the Ca in the original rock to $CaSO_4$. The temperature in the second vessel was also 100°. A portion of the slurry from the second acidulator was recycled to the first acidulator. The remainder was fed to the gypsum filter. The "strong acid" from the filter contained 50% P_2O_5 .

[*ibid*, 72]

Ammonium Polyphosphates: Hans A. Rohlfs and Heinz Schmidt (to Chemische Werke Albert).

U.S. 3,419,349, Dec. 31, 1968, Appl. Jan. 15, 1965; 6 pp.

Catenarly condensed ammonium or ammonium-metal polyphosphates are prepared by heating mixtures of ammonium orthophosphates and urea or its derivatives. The reaction is preferably carried out between 110-450°. For example, a mixture of 26.4 g $(NH_4)_2HPO_4$, 12 g urea, and 19.6 g crystallized H_3PO_4 was heated for two hours at 150°. The reaction product consisted of 45.7 g of crystalline material containing 17.76% N and 62% P_2O_5 . This was heated for an additional two hours at 110-120° while contacting with gaseous NH_3 . The product contained 22% N and 59.1% P_2O_5 , predominantly as ammonium pyrophosphate, soluble at room temperature in H_2O in a wt ratio of about 1:1. In other examples, a mixture of 23 g $NH_4H_2PO_4$ and 14.6 g urea was heated one hour at 300° yielding 20 g of crystalline product containing 14.9% N and 70.8% P_2O_5 ; a mixture of 26.4 g $(NH_4)_2HPO_4$ and 4.4 g oxamide was heated five hours at 200° yielding 23.4 g of a partially glassy product containing 14.1% N and 27.7% P; a mixture of 14 g KH_2PO_4 , 23 g $NH_4H_2PO_4$, and 12 g urea, well ground together, was heated for one hour at 180° yielding 35.3 g of crystalline product containing 6.2% N, 64.8% P_2O_5 , and 21.4% K_2O . Twenty-five other examples are given. Such products are useful in liquid fertilizers and water softeners.

[*ibid*, 74]

Urea-Ammonium Phosphate: L. A. Barry and E. J. Arveson (to International Minerals & Chemical Corp.).

U.S. 3,425,819, Feb. 4, 1969, Appl. May 24, 1965; 2 pp.

High-N fertilizers are prepared by coating urea prills with an ammonium phosphate composition in the presence of excess NH_3 followed by drying. Wet-process

H₃PO₄ containing 40-52% P₂O₅ is ammoniated to prepare a slurry having an NH₃:H₃PO₄ mole ratio in the range 1.32:1-1.35:1 and a H₂O content of 17-18%. The resulting slurry is sprayed on the surface of a rolling bed of prilled urea and recycled fines in a rotary drum while gaseous NH₃ is introduced beneath the bed. The NH₃ is fed in an excess of at least 20% more than that required for the formation of (NH₄)₂HPO₄, preferably a 25-100% or greater excess. The temperature in the drum is preferably 140-160°F. with external heat applied if necessary to maintain that temperature. The product from the drum is dried to 1-3% H₂O in a rotary drier at 140-200°F. and screened to remove fines and oversize. The biuret content is less than 1% and at least 90% of the P₂O₅ is H₂O-soluble. The urea comprises 65-80% of the available N. Loss of urea by hydrolysis is almost completely avoided.

[*ibid*, 75]

Coating Fertilizer Granules: C. D. Goodale and J. A. Frump (to Commercial Solvents Corp.).

U.S. 3,419,379, Dec. 31, 1968, Appl. Sept. 18, 1964; 6 pp.

Fertilizer granules such as NH₄NO₃ are first coated with an acidic material such as superphosphoric acid, H₃PO₄, SO₃, or oleum. The granules are then contacted with a basic material such as NH₃, MgO, or CaO whereby a reaction occurs forming a coating on the surface of the granule. Examples describe the preparation of coatings comprised of CaHPO₄·2H₂O, MgHPO₄·3H₂O, CaSO₄·2H₂O, MgSO₄·7H₂O, (NH₄)₂SO₄, NH₄H₂PO₄, and Ca₃(PO₄)₂. Such coatings prevent caking and some of them can also inhibit dissolution of the fertilizer in the soil.

[*ibid*, 75]

Conditioning of Ammonium Nitrate: D. C. Chappel and G. G. Brown (Fisons Fertilizers Ltd.).

Brit. 1,119,702, July 10, 1968, Appl. Sept. 19, 1964; 3pp. CA 70, 13092.

The caking tendency of granular NH₄NO₃ or ammonium nitrate sulfate is reduced by incorporating into the granules 0.1-5.0% of Al(OH)₃ or a basic Al salt. As an example of the process, a rotary granulator is fed with (NH₄)₂SO₄ crystals, NH₄NO₃ solution, H₂O-soluble Al₂(SO₄)₃, recycled fines, and anhydrous NH₃. The mixture is granulated at elevated temperature (>50°) and the product granules dried. The NH₃

converts the Al₂(SO₄)₃ to Al(OH)₃; the amount of NH₃ used is such as to give a pH of 4.5-5.0 in a 10% solution of the granules. Products made in this way have a crushing strength of 8-12 psi after 7 days storage at 6 psi and 35°, as compared with 80-95 psi crushing strength for untreated granules.

[*ibid*, 2 (5) (1969), 91]

Hydrogen for Ammonia Synthesis: G. Hochgesand (Metallgesellschaft A.-G. and A.G. Linde).

Fr. 1,501, 226, Nov. 10, 1967, Ger. Appl. Nov. 15, 1965; 11 pp. CA 70, 13064.

H for NH₃ synthesis is produced from a crude gas mixture (containing H, CO, CO₂, and S compounds) obtained by the high-pressure (>40 atmosphere) cracking of gaseous or liquid hydrocarbons. The crude gas is scrubbed at ambient temperature and high pressure with an organic polar solvent (Me₂CO or MeOH) to remove H₂S and S compounds, the scrubbed gas is passed to a CO converter to effect the CO shift reaction to CO₂ and H, the converter effluent is cooled to a temperature below the dew point of CO₂, and the cold gas is scrubbed with Me₂CO or MeOH to remove CO₂. A final low temperature scrubbing may be used where residual CO, CH₄, O, and Ar are removed by liquid N. Spent Me₂CO or MeOH from the H₂S and CO₂ scrubbing stages are regenerated by a common recovery system consisting of a combination of rectifying and pressure-let-down columns. The catalyst of the CO shift converter need not be S-resistant since the feed to the converter is desulfurized and the CO₂ removed in the second scrubbing stage is S-free and can be used for the manufacture of urea.

[*ibid*, 91]

Catalyst Support for Ammonia Oxidation: C. D. Keith (to Engelhard Industries, Inc.).

U.S. 3,428,424, Feb. 18, 1969, Appl. Feb. 24, 1965; 7 pp.

In the manufacture of HNO₃ by oxidation of NH₃ in the presence of a Pt catalyst, the usual Pt gauze is replaced by a solid unitary refractory skeletal structure having a plurality of gas flow channels. Pt is deposited on the surfaces of the gas flow channels. Preferred refractory supports are alpha alumina, zirconium silicate, SiO₂·MgO·Al₂O₃, and zirconmullite. The catalyst metal can be applied by dipping

the support in a solution or suspension of the metal, followed by calcining. Less Pt is required, as little as 1% of the Pt required for gauze catalysts. Furthermore, the process eliminates the growth of excrescences occurring on Pt-Rh gauze causing loss of catalytic metal and channeling of gas flow. Pt-group metal alloys that are too hard and brittle for use as gauze, such as 60% Pt 40% Rh, are suitable for use on the refractory support.

[*ibid*, 91]

Catalyst for Steam Reforming of Hydrocarbons: I. Watanabe, et al (to Japan Gasoline Co., Ltd., and Nikki Chemical Co., Ltd).

U.S. 3,429,680, Feb. 25, 1969, Appl. Japan Oct. 15, 1963; 8 pp.

The title catalyst is comprised of 10-30% Ni (present as metal or oxide), and 5-10% (based on Ni content) of a promoter comprised of Cu-Cr oxides and Cu-Cr-Mn oxides on an inorganic oxide support material. For example, 100 g NiCO₃ precipitate (deposited on kieselguhr and containing about 43 g Ni) was mixed with 6 g of an ammonium salt complex of Cu, Cr, and Mn having a mole ratio of 1:1:0.1. The mixture was pelletized and heated at 380°C. in air, followed by heating at 380-400°C. in a stream of H for reduction. The product contained NiO, 54.5; CuO, 2.5; Cr₂O₃, 2.5; MnO, 0.3; and SiO₂, 40.2%. The catalyst was used for steam reforming of butane, cyclohexane, benzene, and olefin-containing gas, respectively. The temperatures were 250-325°C. and the gauge pressures were 0-5.0 kg/sq cm. All conversions were practically complete and were free of C deposits. Test data are tabulated.

[*ibid*, 91]

Inhibition of Urea Hydrolysis: Imperial Chemical Industries Ltd., (by J. R. Anderson).

Brit. 1,142,245, Feb. 5, 1969, Appl. Sept. 8, 1966, 7 pp.

Hydrolysis of urea in the soil causes NH₃ loss and may injure seeds. In the process described, a quinone or polyhydric phenol is mixed with the urea (preferably 0.1-2.0% by wt of the urea) to inhibit hydrolysis. Use of both inhibitors together gives a synergistic effect. In an example, catechol plus 2, 5-dimethyl-p-benzoquinone completely inhibited hydrolysis for 10 days. Without the inhibitors, 50% hydrolysis occurred in 3 days.

[*ibid*, 93]

Concentration of Phosphoric Acids: W. R. Mustain (Armour Agr. Chem. Co.).

U.S. 3,407,862, Oct. 29, 1968, Appl. July 7, 1966, 4 pp.

In the concentration of wet process H_3PO_4 containing metal salts and other impurities, combustion gases are discharged through a vertical, cylindrical dip pipe, which extends downwardly into a frustoconical evaporator and is centered in it to give uniform flow of combustion gases over the H_3PO_4 and upwardly in the chamber. The dehydrator is operated at 690°F. pool temperature with a gas velocity of 1414 ft/minute. The chamber has a flat bottom aligned with the bottom of the dip pipe and has walls extending upwardly and outwardly at a continuous constant angle from the bottom and above the lower end of the dip pipe. The lower end of the dip pipe has a cross-sectional area less than that of the chamber bottom and terminates in a lower edge which is parallel to, and spaced from, the bottom. For the most efficient operation, a minimum ratio of 6.5 should be maintained between dip pipe velocity and cross-sectional area of the annulus between dip pipe outlet and nearest adjacent point of the evaporator.

[*ibid*, 95]

Removal of Sodium Salts from Brines: H. V. Hess and F. C. McCoy (to Texaco, Inc.).

U.S. 3,433,583, Mar. 18, 1969, Appl. June 28, 1967; 4 pp.

Addition of 4, 4'-methylenedianiline to a brine containing over 12% NaCl selectively precipitates Na and Li salts. The process is an economical supplement to fractional crystallization in recovering individual salts such as KCl from ores or natural brines. In an example, a brine containing 7.6% KCl and 16% NaCl was mixed at 70-75° with 500 g of solid 4, 4'-methylenedianiline/liter. The resulting precipitate was filtered off. The filtrate contained 8% KCl and 13% NaCl. The precipitate (filter cake) was mixed at 50° with 2-3 ml of acetone/g of solids. The resulting slurry was filtered, and the filter cake was dried yielding a mixture of 79-9% NaCl and 20-1% KCl. By washing the precipitate with cold water before treatment with acetone, the KCl content was reduced to 5%. The process leaves at least 12% NaCl in the treated brine regardless of the initial concentration above 12% NaCl.

[*ibid*, 97]

Nitric Phosphate Fertilizers: C. H. Davis (to Tennessee Valley Authority).

U.S. 3,436,205, Apr. 1, 1969, Appl. Aug. 25, 1965, 9 pp.

A process is described in which phosphate rock is extracted with HNO_3 and H_3PO_4 or H_2SO_4 , the extraction slurry is reacted with about 85% of the total NH_3 in a preneutralizer tank, and the slurry from the preneutralizer is fed to a rotary ammoniator-granular drum with recycled fines and the remainder of the NH_3 . Potash can be fed to the drum to produce an N-P-K fertilizer. Detailed pilot-plant data are tabulated for the production of 20-20-0, 15-15-15, 26-13-0, and 14-28-0 grades, all having a P_2O_5 water-solubility of 40%.

[*ibid*, 98]

Method of Potash Application on Paddy Rice in Taiwan

According to the water culture studies conducted in Japan, rice needs potassium throughout its whole growth period. The efficiency of absorbed potassium to increase rice grain yield is the highest in the period of 35-45 days before heading. Proper application of potash to paddy field to meet its requirement timely for normal rice growing involves both soil factors and physiological need of the rice plant.

In Taiwan, potassium is not significantly fixed by paddy soils and the leaching loss of added potassium is tremendous especially in the soils having low cation exchange capacity and light texture. Under such conditions, the conventional method of potash application as single basic dressing to paddy rice is most likely to be subject to leaching loss, and therefore, cannot meet the requirement by rice at its later stage of growth. Therefore, the split application of potash to paddy field to meet the timely needs of rice is theoretically better than the conventional single basic dressing. This assumption was repeatedly proved to be sure by field experiments conducted in Taiwan.

The salient findings are as follows:

Split application of potash is in general better than single basic dressing for both the first and second crops of rice on a variety of soils in Taiwan.

At same rate of potash, the larger is the percentage of potash applied as basic, the smaller is the yield of rice.

The best time of top dressing of potash is somewhat at 50 days before heading.

Change of single basic dressing to split application of potash to rice at proper intervals may appreciably contribute to the increase of rice yield which was previously overlooked in experiments and practice.

In the application of the above findings to farm practice, set rules cannot be recommended to obtain the best potash effects and to attain the highest rice yield. It is a delicate problem involving so many factors that the farmer must be on the alert and be flexible in judging the appropriate time for supplying the potash nutrient.

Among various methods of split application of potash investigated, two of them seem to be preferred. The one is to apply 40% of the total rate of potash at the first weeding (15 and 10 days after transplanting at the first and second rice crop, respectively), 40% at the second weeding (30 and 20 days after transplanting at the first and the second rice crop, respectively), and 20% at the panicle formation stage. The others are to apply 40% of the potash at the first weeding, and 60% at the second weeding. In fact, these two recommended methods of potash application are almost similar, except the last two applications (40% and 20%) of potash in the former case are combined into one application at the second weeding in the latter.

Feng, M. P. (Agronomist, T.P.R.F., Taichung Taiwan).

Fertilite (1968), No. 31, July-August, 27-41.

[*The World of NPKS*, No. 35, (1969), 23]

The Value of Urea Nitrate and Urea Phosphate as Nitrogen Fertilisers for Grass and Barley

Urea nitrate, urea phosphate, and a mixture of urea phosphate and urea were tested as nitrogen fertilizers to find whether the presence of the anion decreases the damage urea causes to germinating seeds and seedlings and increases the efficiency of urea by preventing loss of ammonia.

Urea nitrate was compared with ammonium sulphate for grass grown in pots in the glasshouse and with ammonium nitrate for permanent grassland in the field. In the glasshouse, a large dressing of urea nitrate damaged the early growth of grass in sandy-loam soil. On average of sandy-loam and clay-loam soils with a small dressing of fertilizers, grass recovered similar amounts of N from urea nitrate

and ammonium sulphate; with the large dressing it recovered less from urea nitrate.

In the field, 100 and 200 lb N/acre were applied to permanent grassland which was cut twice. The herbage was 'scorched' by the urea nitrate because its solution is very acidic. Urea nitrate at 200 lb N/acre produced less dry matter containing less nitrogen than did ammonium nitrate.

Urea nitrate, urea phosphate and urea phosphate-urea mixture were compared with ammonium nitrate for barley and grass grown in clay-loam and sandy-loam soils. Tests were made of 33, 67 and 100 lb N/acre for barley and 100, 200 and 300 lb N/acre for ryegrass; the fertilizers were applied immediately before sowing. On the light Woburn soil early growth of barley was least good with urea nitrate, which also damaged the early growth of grass.

Urea nitrate was as good a nitrogen fertilizer as ammonium nitrate; urea phosphate and urea phosphate-urea mixture were superior.

Urea nitrate damaged early growth because the urea hydrolysed to give free ammonia. The nitric acid apparently is ineffective in decreasing the damage because it is mobile and diffuses rapidly through a large soil volume.

Urea phosphate does not damage plant growth because the phosphoric acid, being relatively immobile, makes the soil around the granules acid; this causes the urea to diffuse into a larger soil volume before being hydrolysed, and also provides the locally acid soil needed to absorb free ammonia released from the urea.

Both fertilizers have good physical forms. Urea nitrate is a dry crystalline powder and urea phosphate crystallizes easily. Urea phosphate has constant composition and seems a potentially valuable intermediate for producing NP or NPK mixed fertilizers. With present agricultural practice urea nitrate has much less potential use as a fertilizer.

Gasser, J. K. P., and Penny, A. (Rothamsted Experimental Station, Harpenden, Herts.) *J. agric. Sci. Camb.* 1967, 69, 139-146.

[*ibid*]

Talcher Coals

One of the 3 coal-based fertilizer plants proposed during the Fourth plan is going to be installed at Talcher in Orissa. At present there are 3 working collieries in

this area, viz. South Balanda, Talcher and Deulbera—all of the NCDC. A seam, known as Bottom seam, is worked in all these collieries either in full or in part thickness. The bottom seam, a composite coal horizon, is the basal coal horizon and occurs about 105-110 metres above the Talchers. In the southern part of the S. Balanda colliery, the seam appears as a single coaly section with thickness about 5-7 metres. To the dip side in the north, the seam thickens progressively attaining a thickness as high as 20 metres. It shows a tendency of splitting towards the west as also to the east of the area. In the west the seam occurs usually in 3 coaly sections separated by thick shale or sandstone partings. Out of these the bottom coal is important and is proposed to be worked at the new colliery known as Nandira recently opened up by NCDC. Similarly, towards the east as in the Talcher and Deulbera collieries, the seam splits into several coaly sections, out of which the bottom section is important for commercial exploitation in view of its thickness and consistency but it has a tendency of thinning towards the east.

At S. Balanda colliery, the Bottom seam is available at all shallow depths, being on the up-throw side of a major strike fault and is worked in full in the quarry. The present working is confined to the south-eastern part, where the seam is 6-7 metres thick, which appears to be equivalent to the lower part of the Bottom seam, which is clean with occurrence of one or two minor dirt bands. The total quarriable area for the seam is 647.7 acres, out of which the area worked out so far is 80 acres.

At the Talcher colliery, the lower split of the Bottom seam is worked through a pair of shafts under the local nomenclature of main seam which is equivalent to the bottom section of the Bottom seam. The main seam (thickness 5-5.5 metres) is worked in full in the areas of depillaring. However, in areas under development the bottom 3 metres constitute the working section. The seam has been developed in an area of 1338 acres and depillaring has been carried out in some areas with full sand-stowing. Out of the areas under development, nearly half of the property on the eastern side is under fire and sealed and a good portion in the north-west is a present waterlogged. The working of the seam at the moment is thus confined only to the central part. Earlier, the top split of the bottom seam, locally known as the

Top seam, was also worked for some time in the northern and central parts, but now suspended. Recently the colliery property has been extended to include virgin areas covered by prospecting block B on the west and Block C on the south. The present area of the colliery property is thus about 2076 acres.

At the Deulbera colliery the lower split continues and is worked again under the local nomenclature—Main seam. In the west the seam is 4.4 metres thick and thins down to 2.2 metres. Usually, the full thickness of the seam is worked but at places the development is limited to the bottom 3 metres only. The colliery property covers 1138 acres, nearly three-fourths of which are already developed. Dipillaring has also been carried out.

Investigations carried out at the Coal Survey Laboratory (CFRI), Bilaspur have shown that (i) ash at Talcher and Deulbera ranges between 9 and 13 per cent as against 13 to 15 in South Balanda colliery; (ii) there is perceptible increase in the rank of coal from South Balanda in the west to Talcher in the east and Deulbera to the further east; (iii) the coals from Talcher and Deulbera are characterized by relatively higher hydrogen content (5.6-5.8 metres) with consequent higher calorific value (14600 Btu/lb) and more tar yields (145-160 l/te of dry coal) as against those of S. Balanda coals (H 5.2-5.3, per cent C. V. 14200-14350 Btu/lb and tar yield 115-125 l/te); (iv) the bottom 3-3.3 metres portion at S. Balanda is nearly equivalent to the working section of the Main seam at the Talcher and Deulbera collieries; (v) the coal reserves for the Main seam worked at the Talcher and Deulbera collieries amount to about 29 million tonnes while coal production from them is at present 0.456 million; grindability indices are 51 and 41 respectively. S. Balanda colliery has total reserves, all virgin, of about 21 million tonnes (HGI 60).

[*FRI News*, 19 (1) (1969), 20]

National Commission on Agriculture

Sri A. P. Shinde, Minister of State, Ministry of Food & Agriculture, Government of India, stated recently in Parliament that the proposed National Commission would investigate and report on (i) integrated development of agriculture, animal husbandry, farm forestry and inland fisheries in order to ensure the benefits of mixed farming so as to provide a minimum standard of living for even a

small farmer; (2) afforestation as a measure for soil conservation and farm forestry, having a bearing upon fuel needs of the rural areas; (3) the requirements of the new strategy of scientific agriculture in the shape of research support, education, training and extension, statistics and of requisite supplies of good seeds, fertilizers, pesticides, weedicides, fungicides and agricultural machinery; (4) forecast for the decade 1970-71 to 1980-81 about the requirements of short, medium and long term credit of farmers of varying holdings to support the agricultural programmes; (5) the structure of organization of the agricultural services to support the agri-

cultural programmes that may be recommended, defining the relative responsibilities of the Centre and States in this regard, manpower requirements in various classes of services, methods of recruitment and training; (6) the development required in transport, marketing, storage farm mechanization and in processing industries, to support the growth of agricultural production; (7) the special problems of agricultural labour in the context of the new development in agriculture and solutions thereof; (8) the level of basic requirements of social services and amenities in rural sector in order to maintain in the rural areas, the population, necessary for

the developing agricultural programmes, and suggestions for the organization and resources thereof; (9) study of agricultural price problems as policy of incentives for agricultural production; (10) study of agricultural production problems in remote and economically backward areas; (11) development of the economy of the small farmers; and (12) review of land reform programmes and in particular programmes such as consolidation of holdings, which have bearing on the size of the unit of agricultural production.

[*FAI Inf. Serv.*, 10 (23) (1969), 10]

News in Brief

High Pressure Ammonia Recovery

Ammonia from the reactor synthesis gases can be recovered by first absorbing it at high pressure and then recovering it from the water by distillation. During the high pressure ammonia absorption, large amounts of heat are evolved which increase the absorbent temperature. This temperature can increase to such an extent that ammonia will no longer dissolve in liquid. In order to prevent this situation the temperature rise can be limited by increasing the rate of absorbing solution or by introducing inter-cooling apparatus in order to approach isothermal condition.

To obtain more economical solution requires two situations to be examined i.e. varying the amount of liquid, installing inter-cooling exchangers and varying their number. Because of high cost of the high pressure absorbing apparatus required for above application a calculation procedure is required devoid of the usual simplifying assumptions involved in the determination of number of transfer units and the vapour liquid equilibria of the system nitrogen-hydrogen-ammonia-water.

A method of calculating the number of transfer units is presented by G. Guerreri. The method uses equation given by Sherwood and Pigford relating the rates of change of solute and solvent concentration and of temperature as functions of the transfer unit.

The calculation procedure for transfer unit has been applied to a real case calculating the bubble point of the liquids of each transfer unit. The considered absorber is constituted of three transfer packings with two liquor coolers. The working pressure is 190 atm. The liquor is permitted to reach the temperature of 65°C at the end of the first bed, 75°C at the end of the second bed and 60°C at the end of the third bed. The cooler returns the liquor at the temperature of 35°C.

[*Brit. Chem. Engng*, 13 (12) (1968) 1717]

Urea Ammonium Phosphate

TVA has now developed urea ammonium phosphate commercially, as a result of three decades of fertilizer research. It is seeking \$ 3 million for a 40,000 tpa urea/UAP

plant at Musdes Shoals and ultimately proposes to spend \$ 8 million on urea and UAP facilities and \$ 6.5 million to modernize obsolete ammonia facilities.

UAP is notable particularly for its greater flexibility in formulating, whereby a large range of plant nutrient ratios in mixed fertilizers can be obtained. Commercially feasible for UAP is the NPK ratio of 20:20:20 as against the maximum available 16:16:16 ratio now available for conventional fertilizer materials. The higher nutrient content, which can be achieved with UAP, is seen as leading to transportation and distribution savings. The product is granular and lends itself to oil prilling as well as drum and hand granulation.

[*Nitrogen*, No. 58, (1969), 39]

Granular Ammonium Sulphate

TVA has developed a process in pilot plant for producing high quality granular ammonium sulphate in conventional equipment which is similar to their process for granular diammonium phosphate. Sulphuric acid reacts with ammonia in a pre-neutralizer to an NH_3 : H_2SO_4 mole ratio of 1:1. A brick-lined pre-neutralizer and suitable resistant piping are required for withstanding the corrosiveness of the solution. The highly fluid solution from the pre-neutralizer containing less than 10 per cent water is fully ammoniated and granulated in a drum granulator. Granulation occurs at a low pH and a recycle ratio of about 1 lb/lb of product. Final ammoniation of the granules is enhanced by addition of water and an excess of ammonia, which is recovered in scrubbing liquid that is recycled to the pre-neutralizer, chemical heat provides sufficient evaporation of water during granulation to make a drying step unnecessary. The granular product is of low free acid content, has good physical properties and stores well without conditioner. This process can be adapted to the use of by-product sulphuric acid and ammonium sulphate solutions.

SOURCE: [*J. Agri. Food Chem.* 17 (2) (1969), 306.]

[*FAI Abstract. Serv.*, 8 (9) (1969), 10]

Fluid Fertilizers

Ease of application and the ability to carry micronutrients as well as herbicides and pesticides, an advantage not afforded by solids, support the increasing acceptance of fluid fertilizers. There is a production growth from 50,000 tons in 1965 to well over 4 million in 1969. Looking at this growth one can say that liquid fertilizers are likely to become a major factor in the coming restructuring of agricultural production structures. However, Fred D. Lyon, market research director for Central Farmer Fertilizers Co. predicts that suspension fertilizers' share of the market will not be more than 15 to 20% until problems with phosphoric acid are solved. Besides high cost of P_2O_5 , the problem is that most acids today are wet-process, and if they are to be used in suspension, must be concentrated first—an additional step that adds to the cost. Further the high ortho content of wet-process acid makes it harder to keep potash in solution. Low concentrations, coupled with "salting out" tendency of high concentration in cold temperature is another drawback. Although salt out problem has been solved for some formulations, TVA is still working to determine solubilities for polyphosphate mixtures.

Concentration step increases the cost, yet reduced time and labour cost do not offset it entirely. Corrosion is another challenge for fluid fertilizer industry. Steel equipment and tanks are necessary or some form of protective coating must be used.

[*Chem. Engr.*, 76 (10) (1969), 56]

Non-protein Nitrogen in Feedingstuffs

Usage of Non-protein Nitrogen (NPN) compounds in feed-stuffs of animals has been gaining popularity in many countries of the world. The feeding of NPN to replace protein is only possible for ruminants (like cattle) whose rumen flora synthesize protein from NPN. By using NPN other less costly and less nutritious foodstuffs, such as sugar by-products, maize stems, straws and grasses, can also be employed for the cattle. Of the various NPN compounds used such as amino-acids, urea, biuret and

Ammonium salts, urea finds its greatest demand in U.S.A. and U.S.S.R. In U.S.A. 95,000 tonnes of N and in U.S.S.R. 35,000 tonnes of N in the form of grade urea are being used as animal feed. In South Africa biuret is the most commonly used source of NPN.

A large number of tests have been carried out into weight gain, milk yield and N-utilization when protein nitrogen has been replaced by urea nitrogen. Often no differences were apparent between the various N sources, but sometimes urea nitrogen was found to be inferior. This usually occurred when the NPN proportion of the total nitrogen was too high and the ratio composition was unfavourable for NPN utilization. Utilization of urea could be improved when intake is evenly distributed throughout the day.

Usage of NPN and in particular of urea is governed by a number of factors, the most important being the economics of exchanging NPN for other protein sources which also provide additional ingredients such as phosphorus and secondly the dangers associated with urea when it is consumed in large quantities possibly leading to ataxia, a reduced rate of breathing and in some really acute cases death. The use of NPN compounds including urea are advantageous as mixed feedstuffs specially in regions which are dry and where rains are seasonal where the main type of fodder available is over ripe, high-roughage plants with low protein content.

The trend of popularity with NPN compounds including urea in animal feedstuffs are expected to continue and further trials will reveal wider applications.

[*Nitrogen*, No 57, (1969), 30]

Liquid Nitrogen Food Freezer

A new fast freezing food processing system called Cryo-Quick process using liquid nitrogen has been developed by the Air Products Ltd., New Malden, Surrey.

Liquid nitrogen at -196°C is sprayed to the product on the conveyor belt and immediately vaporizes on contact with the food. This ensures a rapid freezing time which is needed to minimize damage of the food cells and to prevent dehydration. A series of fans ensures that the maximum use is made of the cooling effect of the gaseous nitrogen and also direct 99% of the gases towards the loading end. The remainder is diverted to the discharge end where it prevents the ingress of warm air into the tunnel.

The system works on the total loss system, all the gaseous nitrogen being vented. This has the effect of considerably reducing investment costs since there is no requirement for recirculation piping or a refrigeration unit. Maintenance is reduced accordingly.

[*Nitrogen*, No. 57, (1969), 44]

Explosive Grade Ammonium Nitrate

A scheme for the production of 30 tonnes/day of explosive grade ammonium nitrate at a cost of Rs. 35 lakhs has been undertaken at the Sindri unit of FCI Ltd. This chemical will be consumed mostly in the eastern India in meeting the requirement of various explosives used for mining and other purposes. Under this scheme 73-74 per cent ammonium nitrate will be taken up through a pipe to the new plant where it will be concentrated to 96 per cent. The concentrate will be sent to the prilling tower, 70 metres high, for spraying where the prill will be collected and thoroughly screened to remove any trace of ammonium nitrate dust and finally packed. The whole building for ammonium nitrate will be air-conditioned.

[*Sindri News*, 5(4), (1969), 12]

Seminar on Fertilizer Production & Technology

A national seminar on fertilizer production and technology was held at Delhi during December 14-16, 1969. It comprised the following four technical sessions followed by a keynote session: (1) Ammonia Production (2) Urea Production (3) Phosphoric Acid Production (4) Complex Fertilizer Production.

Accord with a German Process

FCI Ltd has signed an agreement with M/s Lurgi of W. Germany at New Delhi on July 26 for the use of Rectisol process for the purification of gases. In this process raw synthesis gas obtained from coal gasification is purified by using methanol as the scrubbing agent.

[*FAI Inf. Serv.*, 10 (15) (1969), 6]

Potash from Distillery Liquor

The Central Salt & Marine Chemicals Research Institute (CSIR), Bhavnagar has worked out a process to recover potassium chloride from distillery spent wash liquor. The laboratory investigations have been confirmed by further

investigations carried out at Daurala Sugar Works, Daurala.

The process consists in passing the settled wash liquor through a column of cation-exchange resin in the sodium form to absorb the cations, potassium, calcium, etc. on the resin. The effluent from the column, containing organic colouring matter, is thrown out as a waste. The cation-exchange resin bed is next eluted with a solution of common salt. The solutions (eluate) obtained is substantially concentrated with respect to potassium chloride. Potassium chloride is separated by making use of the solubility characteristics of the respective salts. The resin bed is reconverted to the sodium form for another operation.

CSMCRI have prepared a tentative cost estimate for a 1 ton/day potash unit, which comes about Rs. 326.00/ton of KCl, while the imported product costs Rs. 450/te.

[*Inf. News Letter, Indus. Liaison & Extn. Serv.* (CSIR, New Delhi), 8 (1) (1969), 12]

Acid-Resistant Fertilizer Bags

Studies have been carried out at the Indian Jute Industries Research Association, Calcutta towards treatment of jute bags with suitable chemicals which can neutralise the acidity from fertilizers packed in them on the expectation that the treated bag will be a cheaper substitute for the conventional polyethylene and bitumen-lined jute bags currently in use. A few chemicals have been identified and a process of treatment worked out from laboratory investigations. The process is based on application of the chemical on raw jute at the batching stage so as to involve no extra processing cost. The process is simple and now requires full-scale mill trial.

[*IJIRA News Letter*, 4 (2) (1969), 2]

Easy Ammonia Process

The present manufacturing process of ammonia relies on high temperatures and extreme pressures. But during recent experiments in USA, ammonia has been made from nitrogen gas at room temperatures and pressures by means of electricity. With further development the idea that nitrogen can be electrically converted to ammonia under mild conditions seems quite attractive.

(Source: GBJHP News, June 1969)
[*Oil Commentary*, 6 (20) (1969), 20]

P. C. Ray Award to P & D Division, FCI Ltd.

The Indian Chemical Manufacturers Association has conferred Sir P. C. Ray Award for 1969 on the Planning & Development Division, Fertilizer Corporation of India Ltd., for its outstanding contribution to the development of catalyst technology relating to fertilizer manufacture.



Dr. K. R. Chakravorty, Director (Technical), P & D Division, FCI Ltd., is Receiving Sir P. C. Ray Award from Dr. Triguna Sen, Minister for Petroleum and Chemicals, Government of India.

Indian Oil Corporation Ltd.,

IOC has now emerged as the largest organization in the country engaged in production and sales in terms of turnover which was over Rs. 526 crores in 1968-69 (20 per cent more than in 1967-68). During the last decade it has set up 3 refineries based on indigenous crudes, 4 major pipeline projects and a broad-based marketing organization operating through 23 main installations, 332 depots and 65 air field stations having a total tankage of 1.24 million kilolitres. During 1968-69 it processed 5.53 million tonnes of crude oil and sold 8.11 kilolitres, which are 27 and 25.5 per cent above last year's performance and transported 1.99 million tonnes (1.37 m. te in 1967-68). Its profit before providing for depreciation and interest amounted to Rs. 32.41 crores (Rs. 22.33 crores in 1967-68) and before taxation and development rebate to Rs. 18.46 crores (Rs. 10.83 crores previous year's).

Nunmati (Gauhati) refinery continued to operate at a level higher than its designed capacity. Gujarat refinery achieved a crude throughput of 2.96 million tonnes, an increase of 54 per cent over last year's and commissioned an Udex plant producing benzene and toluene. Barauni refinery processed 17.67 lakh tonnes of crude and commenced production of IOMEX from January 1969.

IOC has today a participation of 70 per cent in the aviation business and is meeting *inter alia* the refuelling needs of a dozen international air lines. It is now supplying LPG in 27 cities with a total clientele of 15 lakhs.

Oil India Ltd.

1968 has been another year of success. OIL has declared a final dividend of 13 per cent net of all taxes as well as given Rs. 5.73 crores in discount on the sale of the price of crude. The final price of the crude has been brought down further to Rs. 95/tonne from Rs. 97.82, despite an increase of Rs. 2.50/te in the royalty. Sales of crude oil and gas have also shown marginal increase. The repairs in the breaches caused in the crude oil pipeline of the company and also the products line of IOC following the floods in N. Bengal were completed within 24 days.

The demand for petroleum products is expected to rise to 32 million tonnes in 1975 from the present 16 millions; against this, the total indigenous production at present is 5.8 million tonnes. To narrow down this gap ways have to be found to assess the overall potential of the country and its off-shore areas more rapidly.

OIL's share in this effort is confined to (i) 2 exploration licence areas and (ii) to the extent recoveries can be improved upon from the oil accumulation already discovered. Rs. 5 crores have already been spent on exploration in the Ningru (NEFA) and Dum Duma petroleum licence areas. Plans have been drawn up for a further Rs. 5 crores exploration programme. Investigations and sophisticated studies of the probable behaviour of the reservoirs using computers are being used to assist in planning pressure maintenance measures.

Upto 1968 the refineries have been unable to take the full supply of 3.00 million tonnes/yr. of crude available from OIL's oilfields. The two exploratory wells, Kharsang I and Shongking I, drilled in 1968 in NEFA, indicated the existence of hydrocarbons in non-commercial quantities. Kusijan 2 in Dum Duma, completed in May 1969, gave a good flow of oil during preliminary testing but a number of extension wells will have to be drilled to assess its potentiality. Duarmara I, in Dum Duma, the 13th exploratory well is expected to be spudded-in soon. Eight developmental wells were completed in the Mining Lease areas in 1968; wells drilled upto end of May 1969 are 267 of which 210 are oil producers, 10 gas

producers, 23 dry and 24 under test. Crude supplies were: 1592,407 tonnes to Barauni, 767, 284 to Gauhati and 402, 104 to Digboi. The company has under consideration a proposal to produce LPG using run-of-the field and low pressure gas. Deducting crude and gas already produced upto 1.1.69, the reserved, proved and indicated, stand at 43 million tonnes of crude and 37, 955 million cubic metres of gas.

[*Oil Commentary*, 6 (20), (1969), 10]

Hindustan Organic Chemicals

HOC is a Rs. 20-crores public undertaking of the Government of India sited at Rasayani near Panvel, 80 km. from Bombay. Some of the major products which it will manufacture are formaldehyde 37% (15000 te/yr), acetanilide (2000), nitrobenzene (11,000), benzene hexachloride (3,000), mono- o- and p-dichlorobenzene (3500, 300 and 600), meta-aminophenol (750), metanilic acid (1935), nitrobenzene sulphonic acid (2060), aniline (6000), di-, o- and p-nitrochlorobenzene (1500, 820 and 1520), dinitro-benzene (350), m-, o- and p-nitrotoluene (125, 1900 and 1150), hydrogen (600), sulphuric acid (30,000 te; 20,000 te as by-product weak 70% acid) for superphosphate and NPK fertilizer manufacture, and liq. CO₂ (300 te.), obtained as a by-product. As regards the raw materials, it will obtain methanol (7400 te/yr) and nitric acid (10,000) from FCI Ltd. Trombay, benzene and toluene from Hindustan Steel Ltd/Koyali refinery.

The first plant, viz. acetanilide (costing about Rs. 25 lakhs), of this complex has been commissioned with indigenous skill and know-how developed at the National Chemical Laboratory Poona. The production of acetanilide at full stream will result in an import saving of Rs. 65 lakhs with sales value estimated at Rs. 100 lakhs per year. The cost of production viz. Rs. 4100/te compares favourably with the landed cost Rs. 5000 of acetanilide.

[*Chem. Age of India*, 20 (1969), 467]

Fertilizer and Chemicals (T) Ltd.

The company made a net profit of over Rs. 30 lakhs and the remaining loss figure is less than Rs. 10 lakhs now. Loss of production on account of unsteady power supply was of the order of Rs. 40 lakhs. Higher production was achieved in all products except single superphosphate and NPK mixtures. The Fourth Stage Expansion of Udyogamandal division is well under way.

The construction work of Cochin project is progressing well. However there is much delay in the supply of materials by indigenous suppliers which sometime extends to over a year. The second phase of Cochin production is now under consideration by the Government. There is a proposal to establish a capacity of over 137,000 tonnes of P_2O_5 by electrothermal route.

FEDO has secured contract for a 300 tonnes sulphuric acid plant for Travancore Titanium Products. It has also undertaken design, engineering and construction of plants for the Formic Acid project of the Periyar Chemicals at Edayar. FACT Engineering works has undertaken a number of contracts for fabrication and erection works at Trivandrum, Madras, Barauni, etc.

When the Cochin project and the Fourth Stage Expansion of Udyogamandal are completed the company will have a capacity of 240,000 and 45,000 tonnes of nitrogen and P_2O_5 respectively. When the second phase of the Cochin project is also completed the Phosphoric acid capacity will go up to over 180,000 tonnes of P_2O_5 .

[*Lok Udyog*, 3 (7) (1969), 831]

Coal-Oil Hydrogenation Pilot Plant

Dr. V. K. R. V. Rao, Minister of Education and Youth Services, Government of India, inaugurated the commissioning of the high pressure vapour phase catalytic hydrogenation pilot plant at the Central Fuel Research Institute on December 6, 1969.

So far, basic work on the conversion of primary coal oils to finished petroleum products by hydrocracking and hydrotreating technique, both on laboratory and bench-scale, has been carried out at CFRI. However, many of the petroleum crudes and residues can also be so treated for production of fuels to meet specific product demands. The Assam crudes, for example, yield a very poor kerosene and diesel fuel quite unsuitable for normal use and involve considerable loss of middle distillate fractions through sulphur dioxide extraction. Investigations have shown that hydrotreatment of Assam middle distillates yield superior grade kerosene and diesel oil.

So with the commissioning of the vapour phase high pressure hydrogenation pilot plant, it is presumed that process techniques for converting coal oils, petroleum middle distillates, etc to suitable fuels will be developed.



Dr. V. K. R. V. Rao, Union Minister for Education & Youth Services, Pressing the Button to Commission the Pilot Plant.

FCI Signs Agreements with Montecatini

The Fertilizer Corpn. of India signed four licence and know-how agreements with M/s Montecatini Edison of Italy on Oct. 8, 1969 which pertain to ammonia synthesis and urea synthesis sections for the two coal-based plants, viz. at Korba and Ramagudan, for manufacturing fertilizers, recently approved by the Government. The new agreements will provide improved designs for larger plants capacities for urea and ammonia—urea 1500 tonnes/day in two streams and ammonia 900 tonnes/day in single stream. This would be the largest single-stream ammonia plant in India.

There are already 8 agreements with Montecatini Edison connected with the setting up of plants at Durgapur, Cochin, Barauni and Namrup expansion, each with a capacity of 600 tonnes/day of ammonia and 1000 tonnes/day of urea.

[*FAI Inf. Serv.*, 10 (20) (1969), 6]

Reduction of Fertilizer Price

With effect from November 1, 1969, Government of India has reduced the pool issue price of imported ammonium sulphate (coloured and powdery variety) by Rs. 50/te for supplies to State Governments and Union territories. The price inclusive of countervailing import duty for this type of fertilizer is Rs. 424/te for 100 kg. packing. The price to plantations and indigenous

manufacturers, inclusive of countervailing import duty, has been fixed at Rs. 449/te for 100 kg. packing. There has been no change in distribution margin.

[*FAI Inf. Serv.*, 10 (22) (1969), 10]

Sulphuric Acid Process

Newton Chambers Engng Ltd of U. K. have signed a licensing agreement with V/O Licensintorg. Moscow, which covers the design construction and marketing of sulphuric acid plants using CO process system. The process is said to be of particular use where the raw material is pyrites or anhydrite but can also be applied to other feedstocks. It is most advantageous where feedstock produces a dirty gas. It eliminates the need of many gas cleaning stages associated with ore roasting acid plants and to simplify the acid cooling and absorption sections of the plants. Capital cost savings of between 15 and 20 per cent can be achieved with this process over the conventional methods. It has been operated successfully on a commercial scale for more than 7 years and a number of large plants are currently under construction in the USSR.

[*Indian Chem. J.*, 3 (12) (1969), 40]

Three Fertilizer Projects

Government of India have approved installation of 3 coal-based fertilizer projects, viz. at Ramagundam (A.P.), Talcher and Korba, which indicate that the Government will henceforth make better use of indigenous resources, and expertise than it has done so far. In creating new demand for coal, these projects will assist in the reversal of present recession of coal industry and will also help to activate the NCDC and MAMC at Durgapur, which has been working below capacity for lack of orders.

Naphtha through Pipelines

For the first time in India naphtha will soon be delivered through pipelines by Barauni refineries to Indian Explosive Ltd.'s fertilizer plant at Kanpur, a distance of 670 km. Hitherto naphtha from Barauni has been moving to Gorakhpur, Sindri and Rourkela by rail. Barauni is also connected by a pipeline to Haldia, a distance of about 530 km, and so far these pipelines have been carrying motor spirit, kerosene and high speed diesel. Indian Oil Corporation hopes to supply through pipeline naphtha to Durgapur fertilizer plant sometime next year.

[*SIRD News Letter*, 12 (10) (1969), 19]

OBITUARY : Dr. Vincent Sauchelli

We deeply regret to record the passing away of Dr. Vincent Sauchelli, Agricultural Consultant for the National Plant Food Institute, USA in his home at Baltimore on Oct 1, 1969 at the ripe age of 77.

After taking Ph.D. in Chemistry from Massachusetts Institute of Technology, he served as a Director of Agricultural Research in a company at Kuala Lumpur. Later, he served with the Kopper Co at Pittsburgh. From 1934 to 1955 he worked for the Davison Chemical Corp. as head of marketing and development in fertilizers and later as Director of Agricultural Research. He then served for 5 years as a chemical technologist in the National Plant Food Institute, Washington. From 1959, he was consultant to a number of organizations including USAID programme for India on fertilizer technology. He was founder of the Fertilizer Industry Round Table, whose annual proceedings are a mine of informa-

tion on developments in fertilizer technology; he was its chairman since 1951. He was author of two well-known books* on fertilizer technology.

Dr. Sauchelli took interest in the research and other activities of the P & D Division. He used to read TECHNOLOGY regularly and since its very start he took much interest in its development by way of scrutinizing some of its research papers before publication. He participated in the FAI seminar held at Delhi during December 1966 on cost and financing of fertilizer projects in India. He had accepted to participate in the National Seminar on Fertilizer Production and Technology held at Delhi during December 14-16, 1969.

* (i) Chemistry & Technology of Fertilizers; (ii) Fertilizer Nitrogen—Its Chemistry and Technology.

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STATISTICS

TABLE 1—PRODUCTION AND CONSUMPTION OF COMMERCIAL FERTILIZERS

Continent and country	Production July-June						Consumption July-June					
	1966-67			1967-68			1966-67			1967-68		
	Nitro- gen (N)	Phos- phate (P ₂ O ₅)	Potash (K ₂ O)	Nitro- gen (N)	Phos- phate (P ₂ O ₅)	Potash (K ₂ O)	Nitro- gen (N)	Phos- phate (P ₂ O ₅)	Potash (K ₂ O)	Nitro- gen (N)	Phos- phate (P ₂ O ₅)	Potash (K ₂ O)
THOUSAND METRIC TONS												
EUROPE												
Austria	234.5	63.4	—	245.0	70.0	—	89.6	115.0	151.7	100.0	125.0	162.2
Belgium	290.2	424.6	—	350.0	466.7	—	155.0	149.6	176.8	152.0	140.3	166.1
Czechoslovakia	248.0	264.0	—	245.0	275.0	—	278.0	255.6	394.2	320.0	270.0	410.0
France	1,223.5	1,333.0	1,836.6	1,300.0	1,420.0	1,800.0	990.0	1,363.8	1,024.3	1,140.0	1,507.7	1,142.3
Germany												
Democratic Republic	344.1	253.9	2,006.4	336.0	304.6	2,205.6	443.8	325.9	621.1	430.0	350.0	615.9
Federal Republic	1,501.3	860.7	2,064.5	1,559.1	833.8	2,122.5	888.6	791.8	1,076.8	949.8	787.9	1,119.3
Hungary	167.2	131.0	—	188.0	153.0	—	185.3	118.3	83.6	236.6	158.0	119.0
Italy	950.1	516.1	175.1	1,095.8	552.8	162.2	475.3	462.8	173.2	479.7	464.5	178.4
Netherlands	684.1	205.0	0.6	849.3	251.3	0.8	337.4	109.1	130.7	343.5	105.7	128.2
Sweden	120.3	121.6	—	139.4	129.8	—	174.8	118.7	106.8	190.8	128.8	118.7
United Kingdom	732.1	403.1	—	855.0	429.6	—	759.8	439.1	455.7	908.8	466.1	500.9
Yugoslavia	99.9	179.1	—	101.0	203.7	—	198.1	144.7	158.8	206.9	177.5	132.0
U.S.S.R.	3,188.0	1,776.0	2,626.0	3,500.0	1,867.0	2,868.0	2,656.0	1,664.0	1,902.0	3,089.0	1,697.0	2,136.0
NORTH & CENTRAL AMERICA												
Canada	477.9	484.0	1,999.7	550.0	520.0	2,600.0	276.7	374.0	161.6	335.0	400.0	178.3
Cuba	5.0	15.0	—	10.0	10.0	—	105.0	90.0	75.0	120.0	100.0	85.0
Mexico	171.0	83.5	—	190.0	92.8	—	320.0	97.1	22.0	360.0	110.0	28.0
United States	5,546.0	4,697.0	2,811.0	6,152.0	4,868.0	2,456.0	5,467.6	3,896.8	3,303.8	5,977.1	3,874.1	3,453.6
ASIA												
Burma	—	—	—	—	—	—	6.0	1.0	—	20.0	1.1	—
Ceylon	—	—	—	—	—	—	45.0	1.0	40.0	47.0	8.6	45.2
China, Taiwan	158.0	38.8	—	162.6	37.9	—	159.8	37.6	51.9	160.5	38.6	55.9
India	309.0	145.7	—	402.6	207.1	—	830.2	274.6	133.7	1,135.7	438.2	205.8
Israel	24.8	14.1	297.5	25.9	21.5	329.4	24.7	10.6	4.6	28.3	11.8	6.3
Japan	1,789.3	638.9	—	2,041.8	692.9	—	842.0	609.3	611.9	880.7	621.1	634.0
Pakistan	93.1	0.7	—	100.0	1.1	—	170.0	30.5	14.0	230.0	40.0	16.0
China, Mainland	800.0	360.0	100.0	800.0	360.0	100.0	1,850.0	365.0	105.0	1,650.0	365.0	120.0
AFRICA												
Algeria	—	14.8	—	—	16.2	—	17.2	20.8	13.4	14.5	20.1	11.7
Ghana	—	—	—	—	—	—	0.3	1.5	3.5	0.5	1.7	4.3
Rhodesia, Southern	—	20.0	—	—	25.0	—	46.0	25.0	16.7	48.0	28.0	20.0
South Africa	75.0	210.0	—	110.0	267.1	—	97.9	215.0	85.0	130.0	215.0	86.3
Sudan	—	—	—	—	—	—	29.0	0.7	10.0	34.0	0.8	12.0
United Arab Republic	163.0	46.9	—	132.0	55.0	—	243.9	43.7	0.7	220.0	48.0	0.7
Australia	44.0	969.8	—	55.0	981.6	—	113.7	979.7	79.0	133.0	871.0	85.0
WORLD TOTAL	22,300	16,500	14,500	25,000	17,600	15,200	21,800	15,900	13,100	24,300	16,700	14,100

[Monthly Bull. of Agric. Econ. and Stats., FAO., 18 (2) (1969), 16]

TABLE 2—DELIVERIES OF NITROGEN FERTILIZERS TO INDIA & CHINA, '000 TE OF N

	India		China	
	1966-67	1967-68	1966-67	1967-68
Ammonium Sulphate	230.0	251.0	440.0	296.0
Urea	226.0	482.0	324.0	331.0
Ammonium Nitrate	29.0	43.0	152.0	63.0
Ammonium Chloride	—	—	70.0	81.0
Ammonium Phosphate	87.0	165.0	—	—
Others	14.0	34.0	8.0	2.0
Total	586.0	975.0	994.0	773.0

[Nitrogen, No. 58, (1969), 20]

TABLE 3—TRENDS IN FOOD PRODUCTION & POPULATION IN DEVELOPING REGIONS

	Averages				1963	1964	1965	1966	1967
	1948-52	1953-57	1958-62	1963-67					
	Index numbers, average 1952-56 = 100								
<i>Total Food Production¹</i>									
Africa	87	103	116	131	128	130	130	130	138
Far East ²	87	103	122	136	132	136	134	135	144
Latin America	88	104	120	140	132	137	140	141	148
Near East	84	105	124	143	138	139	141	145	151
Total	87	104	121	137	132	136	136	137	145
<i>Population</i>									
Africa	91	102	116	131	125	128	131	134	138
Far East ²	93	102	113	127	121	124	127	130	133
Latin America	90	103	118	136	129	132	136	140	144
Near East	90	103	117	133	126	129	133	136	140
Total	92	102	115	129	123	126	129	133	136
<i>Food Production Per Head¹</i>									
Africa	95	100	101	100	103	102	100	97	100
Far East ²	94	101	108	107	109	110	105	104	108
Latin America	98	101	102	102	102	103	103	101	103
Near East	93	102	107	108	110	107	106	107	108
Total	94	101	106	106	107	108	105	103	106

[Monthly Bull. Agri. Econ. and Stats., FAO, 18 (4) (1969), 2]

¹ Based on United Nations estimates (in some cases adjusted by FAO).² Real product per head from OECD. National accounts of less developed countries. Development Centre, Paris. July 1968, p. 27-30.

TABLE 4—AVERAGE ANNUAL CHANGE IN POPULATION, INCOME PER HEAD, TOTAL DOMESTIC DEMAND FOR FOOD & FOOD PRODUCTION IN INDIVIDUAL DEVELOPING COUNTRIES, 1952-56 TO 1960-64

	Population ¹	Income per Head ²	Estimated total domestic demand for food ³	Food production ⁴	
				Total	per head
Average annual percentage change ⁵					
Food production increased as much as or more than estimated domestic demand					
Venezuela	3.6	2.3	4.5	5.7	2.0
Libya	3.5	1.1	4.1	5.7	2.1
Mexico	3.3	2.7	4.3	5.9	2.5
Malaysia, West	3.1	1.5	3.8	5.0	1.8
Brazil	3.1	2.7	3.9	4.4	1.3
Honduras	3.1	0.8	3.4	3.5	0.2
Thailand	3.0	2.5	4.1	4.3	1.3
Turkey	2.9	1.4	3.7	3.7	0.8
Korea, Rep. of	2.5	2.1	3.5	4.3	1.8
Ceylon	2.5	1.3	3.3	3.4	0.8
Burma	1.9	2.8	3.2	3.3	1.3
Ethiopia	1.6	—	—	3.6	1.8
Cyprus	1.3	1.8	1.8	3.1	1.7
Subtotal	2.8	2.4	4.0	4.4	1.2
Food production increased less than estimated domestic demand but more than population					
Philippines	3.1	0.8	3.6	3.2	0.1
Guatemala	3.1	1.7	3.6	3.1	—
Panama	3.0	3.4	4.1	3.5	0.4
Iran	2.8	—	—	3.2	0.4
Peru	2.7	2.6	4.0	3.1	0.4
United Arab Republic	2.4	3.8	4.3	3.5	1.0
Chile	2.4	1.4	3.0	2.5	—
Pakistan	2.3	1.3	3.2	2.8	0.4
India	2.1	1.7	3.3	2.9	0.7
Tunisia	1.8	1.8	2.3	2.3	0.5
Subtotal	2.3	1.7	3.4	2.9	0.6

[Contd. on p. 253]

TABLE 4 *Contd.*—AVERAGE ANNUAL CHANGE IN POPULATION, INCOME PER HEAD, TOTAL DOMESTIC DEMAND FOR FOOD & FOOD PRODUCTION IN INDIVIDUAL DEVELOPING COUNTRIES, 1952-56 TO 1960-64

	Population ¹	Income per Head ²	Estimated total domestic demand for food ³	Food production ⁴	
				Total	Per head
Average annual percentage change ⁵					
Food production increased less than population					
China (Taiwan)	3.5	3.7	5.2	3.4	-0.1
Colombia	3.2	1.1	3.7	2.5	-0.7
Syria	3.1	1.7	3.9	1.8	-1.4
Iraq	3.0	3.8	5.2	1.5	-1.5
Morocco	2.8	-1.5	2.0	1.5	-1.4
Indonesia	2.2	—	—	1.6	-0.6
Cuba	2.1	3.6	3.3	0.7	-1.4
Algeria	2.0	2.9	3.3	-1.2	-3.0
Argentina	1.8	1.6	2.0	1.5	-0.3
Uruguay	1.4	-0.8	1.3	-0.4	-1.9
Subtotal	2.5	1.0	2.7	1.5	-1.0
Total	2.5	1.8	3.5	3.0	-0.5

(Monthly Bull. Agri. Econ. and Stats., FAO, 18 (4) (1969), 3)

¹ Based on United Nations estimates (in some cases adjusted by FAO).

² Real product per head from OECD. National accounts of less developed countries. Development Centre, Paris. July 1968, p. 27-30.

³ Calculated on basis of previous two columns and of demand elasticities used in FAO, Agricultural commodities—projections for 1975 and 1985. Rome, 1967, Vol. II, p. 28-33.

⁴ FAO index numbers; food production excludes fish but includes cocoa.

⁵ Compound rate; minus sign denotes decrease.

TABLE 5—WHEAT PRICES IN SELECTED COUNTRIES

Year	Argentina	Canada	France	Germany, Fed. Rep. of	Japan	Netherlands	Sweden	U. A. R.	United Kingdom	United States
PRICES IN LOCAL CURRENCIES										
	Pesos/ 100 kg	Dollars/ 60 lb	Francs/ 100 kg	Marks/ 100 kg	1000 yen/ 100 kg	Guilders/ 100 kg	Kronor/ 100 kg	Piastres/ 150 kg	Shillings/ 112 lb	Dollars/ 60 lb
1960	370	1.80	40.0	40.6	3.76	30.1	44.4	400	26.9	1.74
1961	420	1.91	40.6	41.7	3.99	30.2	42.4	400	26.8	1.83
1962	630	1.88	50.2	42.2	4.19	31.0	48.4	400	27.3	2.04
1963	860	1.97	51.2	42.2	4.31	33.0	50.1	400	26.8	1.85
1964	780	1.89	51.0	42.8	4.50	34.5	51.8	400	26.1	1.37
1965	795	2.00	51.8	42.2	4.71	35.8	52.6	400	24.7	1.35
1966	970	1.99	52.3	43.0	5.02	35.8	53.5	400	25.3	1.63
1967	1260	11.70	54.0	38.2	5.24	35.8	50.9	400	25.9	1.39
PRICES IN U.S. CENTS/KG										
1960	4.5	6.7	8.1	9.8	10.4	8.2	8.6	7.7	7.4	6.4
1961	3.8	6.7	8.2	10.4	11.1	8.4	8.2	7.6	7.4	6.7
1962	4.5	6.4	10.2	10.5	11.6	8.6	9.4	6.1	7.5	7.5
1963	6.1	6.7	10.4	10.5	12.0	9.1	9.7	6.1	7.4	6.8
1964	4.7	6.4	10.3	10.7	12.5	9.5	10.0	6.1	7.2	5.0
1965	3.9	6.8	10.5	10.5	13.1	9.9	10.2	6.1	6.8	5.0
1966	3.1	6.8	10.6	10.8	14.0	9.9	10.3	6.1	7.0	6.0
1967	3.6	15.8	10.9	9.6	14.6	9.9	9.8	6.1	6.5	5.1
Export prices										
Year	Chile	India	Mexico	Pakistan	Spain	Australia	Canada	U. S. A.	Import prices	
									United Kingdom	
									1	2
PRICES IN LOCAL CURRENCIES										
	Escudos/ 100 kg	Rupees/ 100 kg	Pesos/ 100 kg	Rupees/ 82.28 lb	Pesetas/ 100 kg	Cents/ 60 lb	Dollars/ 60 lb	Dollars/ 60 lb	£/2240 lb	
1960	7.70	41.7	1,228	16.2	513	135.5	1.67	—	24.7	24.3
1961	7.78	43.8	1,193	16.1	540	143.5	1.90	—	25.8	25.0
1962	9.01	46.4	1,183	14.9	558	145.5	1.96	1.75	25.9	25.7
1963	12.23	45.8	1,235	15.2	593	150.5	2.03	1.79	26.4	25.6
1964	18.03	55.5	1,303	17.7	648	143.5	1.98	1.76	26.8	26.7
1965	25.88	59.7	1,306	16.6	670	144.5	2.00	1.60	25.3	25.4
1966	34.37	71.9	1,238	18.7	671	154.5	2.09	1.83	26.3	27.0
1967	39.22	89.9	1,295	27.0	673	—	1.93	1.70	28.3	26.8
PRICES IN U.S. CENTS/KG										
1960	7.3	8.7	9.8	9.1	8.6	5.6	6.2	—	6.8	6.7
1961	7.4	9.2	9.5	9.1	9.0	5.9	6.6	—	7.1	6.9
1962	—	9.8	9.5	8.4	9.3	6.0	6.7	6.4	7.1	7.1
1963	—	9.6	9.9	8.6	9.9	6.2	6.9	6.6	7.3	7.0
1964	—	11.7	10.4	9.9	10.8	5.9	6.7	6.5	7.4	7.4
1965	—	12.5	10.4	9.4	11.2	5.9	6.8	5.9	7.0	7.0
1966	—	11.6	9.9	10.5	11.2	6.4	7.1	6.7	7.3	7.4
1967	—	11.9	10.4	15.2	11.0	—	6.6	6.2	7.4	7.3

[Monthly Bull. Agri. Econ. and Stats, FAO, 18 (3) (1969), 49]

TABLE 6—EXPORTS BY MAIN SUPPLYING REGIONS OF
FERTILIZER NITROGEN

('000 TONNES N)

	1959-60	1967-68	Change
West Europe	1,616	2,275	+ 68%
Japan	354	1,053	+197%
U.S.A.	104	589	+467%
East Europe	150	450	+200%
Chile	174	95	- 45%
Arabian Gulf	—	50	—
Others	197(a)	404(b)	+105%
Total	2,595	5,366	+107%

(a) Primarily Canada

(b) Primarily Canada, Trinidad, Aruba and Taiwan

TABLE 7—EXPORTS OF NITROGEN FERTILIZERS
('000 TONNES N)

	1966-67	1967-68	Change
Ammonium Sulphate	1,510	1,436	- 5%
Ammonium Nitrate	842	927	+ 10%
Calcium Nitrate	155	144	- 7%
Sodium Nitrate	101	86	- 15%
Calcium Cyanamide	15	9	- 40%
Urea	1,288	1,747	+ 36%
Complex Fertilizers	633	873	+ 38%
Others	195	144	- 26%
Total	4,749	5,366	+ 13%

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